LOW VOLATILE SOLVENT-BASE PRECURSOR FOR NANOPOROUS AEROGEL

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Low volatility solvent-based precursors for nanoporous aerogels
Wenig fluchtiges Losungsmittel enthaltender Vorlaufer fur nanoporoses Aerogel
Precurseurs pour aerogels nanoporeuse a base de solvent peu volatile

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An aerogel precursor sol is disclosed herein. This aerogel precursor sol comprises a metal-based aerogel precursor reactant and a first solvent comprising a polyol; wherein, the molar ratio of the first solvent molecules to the metal atoms in the reactant is at least 1 : 16 . Preferably, the first solvent is glycerol. Preferably, the aerogel precursor reactant may selected from the group consisting of metal alkoxides, at least partially hydrolyzed metal alkoxides, particulate metal oxides, and combinations thereof. Typically, the molar ratio of the first solvent molecules to the metal atoms in the reactant is no greater than 12 : 1, and preferably, the molar ratio of the first solvent molecules to the metal atoms in the reactant is between 1 : 2 and 12 : 1. In some embodiments, the molar ratio of the first solvent molecules to the metal atoms in the reactant is between 2.5 :1 and 12:1. In some embodiments, the first solvent comprises a glycol. In some embodiments, the reactant is tetraethoxysilane that may be at least partially hydrolyzed. In some embodiments, the first polyol is selected from the group consisting of 1,2,4-butanetriol; 1,2,3- butanetriol; 2 methyl-propanetriol; and 2-(hydroxymethyl)-1,3-propanediol; 1-4, 1-4, butanediol; and 2-methyl-1,3-propanediol, and combinations thereof. This invention allows controlled porosity thin film nanoporous aerogels to be deposited, gelled, aged, and dried without atmospheric controls. In another aspect, this invention allows controlled porosity thin film nanoporous aerogels to be deposited, gelled, rapidly aged at an elevated temperature, and dried with only passive atmospheric controls, such as limiting the volume of the aging chamber.

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Specification:

This invention pertains generally to precursors for nanoporous (fine-pored) aerogel fabrication, and more particularly to precursors suitable for subcritical and supercritical drying of bulk and thin film aerogels.

BACKGROUND OF THE INVENTION

Aerogels are porous silica materials which can be used for a variety of purposes including as films (e.g. as electrical insulators on semiconductor devices or as optical coatings) or in bulk (e.g. as thermal insulators). For ease of discussion, the examples herein will be mainly of usage as electrical insulators

on semiconductor devices.

Semiconductors are widely used in integrated circuits for electronic devices such as computers and televisions. Semiconductor and electronics manufacturers, as well as end users, desire integrated circuits which can accomplish more in less time in a smaller package while consuming less power. However, many of these desires are in opposition to each other. For instance, simply shrinking the feature size on a given circuit from 0.5 microns to 0.25 microns can increase energy use and heat generation by 30%. Miniaturization also generally results in increased capacitive coupling, or crosstalk, between conductors which carry signals across the chip. This effect both limits achievable speed and degrades the noise margin used to insure proper device operation. One way to reduce energy use/heat generation and crosstalk effects is to decrease the dielectric constant of the insulator, or dielectric, which separates conductors. US Patent 5,470,802, issued to Gnade et al., provides background on several of these schemes.

A class of materials, nanoporous dielectrics, includes some of the most promising new materials for semiconductor fabrication. These dielectric materials contain a solid structure, for example of silica, which is permeated with an interconnected network of pores having diameters typically on the order of a few nanometers. These materials may be formed with extremely high porosities, with corresponding dielectric constants typically less than half the dielectric constant of dense silica. And yet despite their high porosity, it has been found that nanoporous dielectrics may be fabricated which have high strength and excellent compatibility with most existing semiconductor fabrication processes. Thus nanoporous dielectrics offer a viable low-dielectric constant replacement for common semiconductor dielectrics such as dense silica.

The preferred method for forming nanoporous dielectrics is through the use of sol-gel techniques. The word sol-gel does not describe a product but a reaction mechanism whereby a sol, which is a colloidal suspension of solid particles in a liquid, transforms into a gel due to growth and interconnection of the solid particles. One theory is that through continued reactions within the sol, one or more molecules in the sol may eventually reach macroscopic dimensions so that it/they form a solid network which extends substantially throughout the sol. At this point (called the gel point), the substance is said to be a gel. By this definition, a gel is a substance that contains a continuous solid skeleton enclosing a continuous liquid phase. As the skeleton is porous, the term "gel" as used herein means an open-pored solid structure enclosing a pore fluid.

One method of forming a sol is through hydrolysis and condensation reactions, which can cause a multifunctional monomer in a solution to polymerize into relatively large, highly branched particles. Many monomers suitable for such polymerization are metal alkoxides. For example, a tetraethoxysilane (TEOS) monomer may be partially hydrolyzed in water by the reaction Reaction conditions may be controlled such that, on the average, each monomer undergoes a desired number of hydrolysis reactions to partially or fully hydrolyze the monomer. TEOS which has been fully hydrolyzed becomes Si(OH) 4)). Once a molecule has been at least partially hydrolyzed, two molecules can then link together in a condensation reaction, such as or to form an oligomer and liberate a molecule of water or ethanol. The Si-O-Si configuration in the oligomer formed by these reactions has three sites available at each end for further hydrolysis and condensation. Thus, additional monomers or oligomers can be added to this molecule in a somewhat random fashion to create a highly branched polymeric molecule from literally thousands of monomers. An oligomerized metal alkoxide, as defined herein, comprises molecules formed from at least two alkoxide monomers, but does not comprise a gel.

Sol-gel reactions form the basis for xerogel and aerogel film deposition. In a typical thin film xerogel process, an ungelled precursor sol may be applied (e.g., spray coated, dip-coated, or spin-coated) to a substrate to form a thin film on the order of several microns or less in thickness, gelled, and dried to

form a dense film. The precursor sol often comprises a stock solution and a solvent, and possibly also a gelation catalyst that modifies the pH of the precursor sol in order to speed gelation. During and after coating, the volatile components in the sol thin film are usually allowed to rapidly evaporate. Thus, the deposition, gelation, and drying phases may take place simultaneously (at least to some degree) as the film collapses rapidly to a dense film. In contrast, an aerogel process differs from a xerogel process largely by avoiding pore collapse during drying of the wet gel. Some methods for avoiding pore collapse include wet gel treatment with condensation-inhibiting modifying agents (as described in Gnade 802) and supercritical pore fluid extraction.

SUMMARY OF THE INVENTION

Between aerogels and xerogels, aerogels are the preferable of the two dried gel materials for semiconductor thin film nanoporous dielectric applications. Typical thin film xerogel methods produce films having limited porosity (up to 60% with large pore sizes, but generally substantially less than 50% with pore sizes useful in submicron semiconductor fabrication). While some prior art xerogels have porosities greater than 50%; these prior art xerogels had substantially larger pore sizes (typically above 100 nm). These large pore size gels have significantly less mechanical strength. Additionally, their large size makes them unsuitable for filling small (typically less than 1 (mu)m, and potentially less than 100 nm) patterned gaps on a microcircuit and limits their optical film uses to only the longer wavelengths. A nanoporous aerogel thin film, on the other hand, may be formed with almost any desired porosity coupled with a very fine pore size. Generally, as used herein, nanoporous materials have average pore sizes less than about 25 nm across, but preferably less than 20 nm (and more preferably less than 10 nanometers and still more preferably less than 5 nanometers). In many formulations using this method, the typical nanoporous materials for semiconductor applications may have average pore sizes at least 1 nm across, but more often at least 3 nm. The nanoporous inorganic dielectrics include the nanoporous metal oxides, particularly nanoporous silica.

In many nanoporous thin film applications, such as aerogels and xerogels used as optical films or in microelectronics, the precise control of film thickness and aerogel density are desirable. Several important properties of the film are related to the aerogel density, including mechanical strength, pore size and dielectric constant. It has now been found that both aerogel density and film thickness are related to the viscosity of the sol at the time it is applied to a substrate. This presents a problem which was heretofore unrecognized. This problem is that with conventional precursor sols and deposition methods, it is extremely difficult to control both aerogel density and film thickness independently and accurately.

Nanoporous dielectric thin films may be deposited on patterned wafers, often over a level of patterned conductors. It has now been recognized that sol deposition should be completed prior to the onset of gelation to insure that gaps between such conductors remain adequately filled and that the surface of the gel remains substantially planar. To this end, it is also desirable that no significant evaporation of pore fluid occur after gelation, such as during aging. Unfortunately, it is also desirable that the gel point be reachable as soon after deposition as possible to simplify processing, and one method for speeding gelation of thin films is to allow evaporation to occur. It is recognized herein that a suitable precursor sol for aerogel deposition should allow control of film thickness, aerogel density, gap fill and planarity, and be relatively stable prior to deposition, and yet gel relatively soon after deposition and age without substantial evaporation.

A method has now been found which allows controlled deposition of aerogel thin films from a multi-solvent precursor sol. In this method, sol viscosity and film thickness may be controlled relatively independently. This allows film thickness to be rapidly changed from a first known value to a second known value which can be set by solvent ratios and spin conditions, thus keeping film thickness largely

independent of aerogel density and allowing rapid gelation. However, at the same time, the solid:liquid ratio present in the film at drying (and therefore the aerogel density) can be accurately determined in the precursor sol prior to deposition, independent of spin conditions and film thickness.

Even with this novel separation of the deposition problem into viscosity control and density control subproblems, our experience has been that thin film sol-gel techniques for forming xerogels and aerogels generally require some method, such as atmospheric control, to limit evaporation before drying, such as after gelation and during aging. In principle, this evaporation rate control can be accomplished by controlling the solvent vapor concentration above the wafer. However, our experience has shown that the solvent evaporation rate is very sensitive to small changes in the vapor concentration and temperature. In an effort to better understand this process, we have modeled the isothermal vaporization of several solvents from a wafer as a function of percent saturation. The ambient temperature evaporation rates for some of these solvents are given in Figure 1. For evaporation to not be a processing problem, the product of the evaporation rate and processing time (preferably on the order of minutes) should be significantly less than the film thickness. This suggests that for solvents such as ethanol, the atmosphere above the wafer would have to be maintained at over 99% saturation. However, there can be problems associated with allowing the atmosphere to reach saturation or supersaturation. Some of these problems are related to condensation of an atmospheric constituent upon the thin film. Condensation on either the gelled or ungelled thin film has been found to cause defects in an insufficiently aged film. Thus, it is generally desirable to control the atmosphere such that no constituent is saturated.

Rather than using a high volatility solvent and precisely controlling the solvent atmosphere, we have discovered that a better solution is to use a low volatility solvent with less atmospheric control. Upon investigating this premise, we have discovered that glycerol makes an excellent solvent.

The use of glycerol allows a loosening (as compared to prior art solvents) of the required atmospheric control during deposition, gelation, and/or aging. This is because, that even though saturation should still preferably be avoided, the atmospheric solvent concentration can be lowered without excessive evaporation. Figure 2 shows how the evaporation rate of glycerol varies with temperature and atmospheric solvent concentration. It has been our experience that, with glycerol, acceptable gels can be formed by depositing, gelling and aging in an uncontrolled or a substantially uncontrolled atmosphere.

In the production of nanoporous dielectrics it is preferable to subject the wet gel thin film to a process known as aging. Hydrolysis and condensation reactions do not stop at the gel point, but continue to restructure, or age, the gel until the reactions are purposely halted. It is believed that during aging, preferential dissolution and redeposition of portions of the solid structure produce beneficial results, including higher strength, greater uniformity of pore size, and a greater ability to resist pore collapse during drying. Unfortunately, we have now found that conventional aging techniques used for bulk gels are poorly suited for aging thin films in semiconductor processing, partly because they generally require liquid immersion of the substrate and partly because they require days or even weeks to complete. One aspect of this invention includes a vapor phase aging technique that avoids liquid immersion or premature drying of the wet gel thin film and that, surprisingly, can age such a thin film in a matter of minutes.

Again, aerogels are nanoporous materials which can be used for a variety of purposes including as films or in bulk. It should be noted, however, the problems incurred in film fabrication processing is so different from bulk processing problems, that, for practical purposes, film processing is not analogous to bulk processing.

Generally, we have now found that aging in a saturated atmosphere avoids the difficulties encountered with liquid immersion aging. Furthermore, this aspect of the invention provides several approaches for

aging wet gels at increased temperatures. These methods may be used even when the wet gel originally contains low boiling point pore liquids. However, they work better with low volatility solvents. Finally, this aspect of the invention provides for adding an optional vapor phase aging catalyst to the aging atmosphere to speed aging.

Aging a wet gel in thin film form is difficult, as the film contains an extremely small amount of pore fluid that should be held fairly constant for a period of time in order for aging to occur. If pore fluid evaporates from the film before aging has strengthened the network, the film will tend to densify in xerogel fashion. On the other hand, if excess pore fluid condenses from the atmosphere onto the thin film before the network has been strengthened, this may locally disrupt the aging process and cause film defects.

Thus, we now know that some method of pore fluid evaporation rate control during aging is beneficial to aerogel thin film fabrication. In principle, evaporation rate control during aging can be accomplished by actively controlling the pore fluid vapor concentration above the wafer. However, the total amount of pore fluid contained in, for instance, a 1 mm thick 70% porous wet gel deposited on a 150 mm wafer is only about 0.012 mL, an amount that would easily fit in a single 3 mm diameter drop of fluid. Typical thin films used for nanoporous dielectrics on semiconductor wafers are approximately 1000 times thinner. Thus, actively controlling the pore fluid vapor concentration (by adding or removing solvent to the atmosphere) to allow no more than, e.g., 1%, or less, pore fluid evaporation during aging presents a difficult proposition; the surface area of the thin film is high and the allowable tolerance for pore fluid variations is extremely small. In particular, evaporation and condensation control are especially important for rapid aging at elevated temperature, where film production processes have heretofore apparently not been practically possible.

We have overcome the evaporation rate control problem by not attempting to actively control pore fluid vapor concentration above a wafer at all. Instead, the wafer is processed in an extremely low-volume chamber, such that through natural evaporation of a relatively small amount of the pore fluid contained in the wet gel film, the processing atmosphere becomes substantially saturated in pore fluid. Unless the wafer is cooled at some point in a substantially saturated processing atmosphere, this method also naturally avoids problems with condensation, which should generally be avoided, particularly during high temperature processing.

A metal-based nanoporous aerogel precursor sol is disclosed herein. This nanoporous aerogel precursor sol comprises a metal-based aerogel precursor reactant and a first solvent comprising a first polyol; wherein, the molar ratio of the first solvent molecules to the metal atoms in the reactant is at least 1 : 16 . Preferably, the first polyol is glycerol. Preferably, the aerogel precursor reactant may be selected from the group consisting of metal alkoxides, at least partially hydrolyzed metal alkoxides, particulate metal oxides, and combinations thereof. Typically, the molar ratio of the first solvent molecules to the metal atoms in the reactant is no greater than 12 : 1, and preferably, the molar ratio of the first solvent molecules to the metal atoms in the reactant is between 1 : 2 and 12 : 1. In some embodiments, the molar ratio of the first solvent molecules to the metal atoms in the reactant is between 2.5 :1 and 12:1. In this method, it is also preferable that the nanoporous dielectric has a porosity greater than 60% and an average pore diameter less than 25 nm. In some embodiments, the aerogel precursor also comprises a second solvent. Preferably, the second solvent has a boiling point lower than glycerol's. In some embodiments, the second solvent may be ethanol. In some embodiments, the first solvent also comprises a glycol, preferably selected from the group consisting of ethylene glycol, 1,4 butylene glycol, 1,5 pentanediol, and combinations thereof. In some embodiments, the first polyol is selected from the group consisting of 1,2,4-butanetriol; 1,2,3- butanetriol; 2 methyl-propanetriol; and 2-(hydroxymethyl)-1,3-propanediol; 1-4, 1-4, butanediol; and 2-methyl-1,3-propanediol, and combinations thereof. In some embodiments, the first polyol is a glycol selected from the group consisting of ethylene glycol, 1,4

butylene glycol, 1,5 pentanediol, and combinations thereof.

Thus, this invention allows controlled porosity thin film nanoporous aerogels to be deposited, gelled, aged, and dried without atmospheric controls. In another aspect, this invention allows controlled porosity thin film nanoporous aerogels to be deposited, gelled, rapidly aged at an elevated temperature, and dried with only passive atmospheric controls, such as limiting the volume of the aging chamber.

A method for forming a thin film nanoporous dielectric on a semiconductor substrate is disclosed herein. This method comprises the steps of providing a semiconductor substrate and depositing an nanoporous aerogel precursor sol upon the substrate. This aerogel precursor sol comprises a metal-based aerogel precursor reactant and a first solvent comprising glycerol; wherein, the molar ratio of the molecules of glycerol to the metal atoms in the reactant is at least 1 : 16 . The method further comprises allowing the deposited sol to create a gel, wherein the gel comprises a porous solid and a pore fluid; and forming a dry, nanoporous dielectric by removing the pore fluid in a drying atmosphere without substantially collapsing the porous solid. In this method, the pressure of the drying atmosphere during the forming step is less than the critical pressure of the pore fluid, preferably near atmospheric pressure.

Preferably, the aerogel precursor reactant may be selected from the group consisting of metal alkoxides, at least partially hydrolyzed metal alkoxides, particulate metal oxides, and combinations thereof. Preferably, the aerogel precursor reactant comprises silicon. In some embodiments, the aerogel precursor reactant is TEOS. Typically, the molar ratio of the molecules of glycerol to the metal atoms in the reactant is no greater than 12 : 1, and preferably, the molar ratio of the molecules of glycerol to the metal atoms in the reactant is between 1 : 2 and 12 : 1. In some embodiments, the molar ratio of the molecules of glycerol to the metal atoms in the reactant is between 2.5 :1 and 12:1. In this method, it is also preferable that the nanoporous dielectric has a porosity greater than 60% and an average pore diameter less than 25 nm. In some embodiments, the aerogel precursor also comprises a second solvent. Preferably, the second solvent has a boiling point lower than glycerol's. In some embodiments, the second solvent may be ethanol. In some embodiments, the first solvent also comprises a glycol, preferably selected from the group consisting of ethylene glycol, 1,4-butylene glycol, 1,5-pentanediol, and combinations thereof. After aging but before drying, in some embodiments, the aging fluid is replaced by a drying fluid. This allows, e.g., rapid, lower temperature (e.g., room temperature) drying with a fluid that evaporates faster and has a suitably low surface tension. Examples of drying fluids include heptane, ethanol, acetone, 2-ethylbutyl alcohol and some alcohol-water mixtures.

Thus, this invention allows controlled porosity thin film nanoporous aerogels to be deposited, gelled, aged, and dried without atmospheric controls. In another aspect, this invention allows controlled porosity thin film nanoporous aerogels to be deposited, gelled, rapidly aged at an elevated temperature, and dried with only passive atmospheric controls, such as limiting the volume of the aging chamber.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention, including various features and advantages thereof, may be best understood with reference to the following drawings, wherein:

Figure 1 contains a graph of the variation of evaporation rate with saturation ratio and solvent type.

Figure 2 contains a graph of the evaporation rate for glycerol a function of temperature and atmospheric saturation ratio.

Figure 3 contains a graph of the theoretical relationship between porosity, refractive index, and dielectric

constant for nanoporous silica dielectrics.

Figure 4 contains a graph of the change in gel times (without solvent evaporation) for bulk ethylene glycol-based gels as a function of base catalyst

Figure 5 contains a graph of the variation of modulus with density for a non-glycol-based gel and an ethylene glycol-based gel.

Figure 6 contains a graph showing the distribution of pore sizes of a bulk glycerol-based nanoporous dielectric according to the present invention.

Figure 7 contains a graph of the evaporation rate for ethylene glycol as a function of temperature and atmospheric saturation ratio.

Figure 8 contains a graph showing the change in vapor pressure with temperature.

Figure 9 contains a graph showing the shrinkage of a thin film when dried in a 5 mm thick container.

Figure 10 contains a graph showing the shrinkage of a thin film when dried in a 1 mm thick container.

Figures 11A-11B contain graphs of the viscosity variation as a function of alcohol volume fraction for some ethylene glycol/alcohol and glycerol/alcohol mixtures.

Figures 12A-12B contain cross-sections of a semiconductor substrate at several points during deposition of a thin film according to the present invention.

Figure 13 is a flow chart of a deposition process for a nanoporous dielectric according to the present invention.

Figure 14 contains a graph of the theoretical molar ratio of glycerol molecules to metal atoms vs. porosity of a nanoporous dielectric according to the present invention.

Figure 15 contains a graph of relative film thickness and relative film viscosity as a function of time for one embodiment of the present invention.

Figures 16A and 16B contain, respectively, a cross-sectional and a plan view of a sol-gel thin film processing apparatus according to the present invention.

Figure 16C contains a cross-sectional view of the same apparatus in contact with a substrate.

Figures 17A and 17B contain, respectively, cross-sectional views of another apparatus according to the present invention, empty and enclosing a substrate.

Figures 18A and 18B contain, respectively, cross-sectional views of yet another apparatus according to the present invention, empty and enclosing a substrate.

Figures 19A, 19B and 19C contain cross-sectional views of additional apparatus configurations which illustrate other aspects of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Typical sol-gel thin film processes produce gels which collapse and densify upon drying, thus forming xerogels having only a few percent porosity. Under the uncontrolled drying conditions of xerogel film formation, it has been neither critical nor possible to completely separate the deposition, aggregation, gelation, and drying steps during formation of the thin film, as the entire process may be completed in a few seconds. However, it has now been found that such methods are generally unsuited for depositing high porosity thin films with a controllable low density; because in an aerogel type drying process, the film remains substantially undensified after drying, its final density is largely determined by the solid:liquid ratio in the film at the gel time. It has now been discovered that the following criteria are desirable for aerogel thin film deposition, particularly where the thin film is required to planarize and/or gap fill a patterned wafer:

1) an initial viscosity suitable for spin-on application

2) stable viscosity at deposition

3) stable film thickness at gel time

4) a predetermined solid:liquid ratio at gel time

5) gelation shortly after deposition No prior art precursor sol and method have been found which meet these conditions. However, in accordance with the present invention, it has now been found that a sol prepared with at least two solvents in specific ratios may be used to meet these conditions.

The method of depositing and gelling such a precursor sol can be best understood with reference to Figure 15.

As shown in Figure 15 for time t=0, a multi-solvent precursor sol may be spun onto a wafer at an initial film thickness D0 and an initial viscosity h0. This is preferably done in a controlled atmosphere having a partial pressure of the low volatility solvent which greatly retards evaporation of the low volatility solvent from the wafer. Thus after spin-on application, the high volatility solvent is preferentially removed from the wafer during evaporation time period T1 while the low volatility solvent is maintained, thereby decreasing the film thickness to D1. Viscosity also changes during this time to h1, preferably due primarily to the removal of solvent. Ideally, little cross-linking of polymeric clusters in the sol occurs during this time. At the end of T1, substantially all of the high volatility solvent should be evaporated, at which time film thickness should stabilize or proceed to shrink at a much reduced rate, thereby providing a predetermined liquid:solid ratio and thickness for the thin film at gel time.

Time period T2 has the primary purpose of providing separation between the endpoint of evaporation time period T1 and the gel point which occurs during gelation time period T3. Preferably, time period T2 is greater than 0. However, some precursors, particularly those with solvents such as glycerol, that promote faster gelation, will gel toward the end of period T1. Additionally, during time period T1 or T2 a vapor-phase catalyst such as ammonia may be introduced into the controlled atmosphere. This catalyst may diffuse into the thin film, further activating the sol and promoting rapid cross-linking. Although little or no evaporation preferably takes place during T2, viscosity should begin to increase substantially as cross-linking continues to link polymeric clusters.

Evaporation after the gel point may result in poor gap-fill and planarity for patterned wafers. Consequently, after gelation time period T3, film thickness is preferably held nearly constant until the gel point has passed by limiting evaporation. Sometime during time period T3, a marked change in viscosity occurs as the sol nears the gel point, where large polymeric clusters finally join to create a

spanning cluster which is continuous across the thin film.

Several advantages of this new approach are apparent from Figure 15. Sol viscosity and film thickness are both allowed to change rapidly, but generally not at the same time. Also, film thickness is changed from a first known value to a second known value which can be independently set by solvent ratios and spin conditions. Using this method, a low viscosity film may be applied, quickly reduced to a preset thickness, and rapidly gelled at a desired density.

The preceding paragraphs teach a method of varying the precursor sol viscosity independently of the dried gel density. However, it still leaves open the question of which solvents are most appropriate. Our experience shows that the solvent evaporation rate for traditional aerogel solvents is very sensitive to small changes in the vapor concentration and temperature. In an effort to better understand this process, we have modeled isothermal solvent vaporization from a wafer as a function of percent saturation. This modeling is based on mass transfer theory. Transport Phenomena, (particularly Chapters 16 and 17) by R. B. Bird, W. E. Stewart, and E. N. Lightfoot, is a good reference for mass transfer theory. These calculations were performed for a range of solvents. The ambient temperature evaporation rates for some of these solvents are given in Figure 1. For evaporation to not be a processing problem, the product of the evaporation rate and processing time (preferably on the order of minutes) should be significantly less than the film thickness. This suggests that for solvents such as ethanol, the atmosphere above the wafer would have to be maintained at over about 99% saturation. However, there can be problems associated with allowing the atmosphere to reach saturation or supersaturation. Some of these problems are related to condensation of an atmospheric constituent upon the thin film. Condensation on either the gelled or ungelled thin film has been found to cause defects in an insufficiently aged film. Thus, it is generally desirable to control the atmosphere such that no constituent is saturated.

Rather than using a high volatility solvent and precisely controlling the solvent atmosphere, we have discovered that a better solution is to use a low volatility solvent with less atmospheric control. Upon investigating this premise, we have discovered that glycerol makes an excellent solvent.

The use of glycerol allows a loosening (as compared to prior art solvents) of the required atmospheric control during deposition and/or gelation. This is because, that even though saturation should still preferably be avoided, the atmospheric solvent concentration can be lowered without excessive evaporation. Figure 2 shows how the evaporation rate of glycerol varies with temperature and atmospheric solvent concentration. It has been our experience that, with glycerol, acceptable gels can be formed by depositing and gelling in an uncontrolled or a substantially uncontrolled atmosphere. In this most preferred approach, (a substantially uncontrolled atmosphere) atmospheric controls, if any, during deposition and gelation are typically limited to cleanroom temperature and humidity controls, although the wafer and/or precursor sol may have independent temperature controls.

One attractive feature of using glycerol as a solvent is that at ambient temperature, the evaporation rate is sufficiently low so that several hours at ambient conditions will not yield dramatic shrinkage for thin films. It has been our experience that with glycerol, acceptable gels can be formed by depositing, gelling, and aging in an uncontrolled or a substantially uncontrolled atmosphere. With glycerol, the ambient temperature evaporation rate is sufficiently low so that several hours at ambient conditions will not yield dramatic shrinkage for thin films. It has also been our experience that with ethylene glycol, acceptable gels can be formed by depositing, and gelling an uncontrolled or a substantially uncontrolled atmosphere. With ethylene glycol, the ambient temperature evaporation rate is higher than glycerol, but still sufficiently low so that several minutes at ambient conditions will not yield dramatic shrinkage for thin films. However, the ethylene glycol-based sols have significantly lower viscosities than comparable glycerol-based sols, thus simplifying deposition. Also, the pore fluids in glycerol-based sols have significantly higher surface tensions than comparable ethylene glycol-based sols, thus making low

shrinkage drying more difficult.

In addition to serving as a low vapor pressure and water-miscible solvent, ethylene glycol and glycerol may also participate in sol-gel reactions. Although the exact reactions in this process have not been fully studied, some reactions can be predicted. If tetraethoxysilane (TEOS) is employed as a precursor, ethylene glycol can exchange with the ethoxy groups:

Similarly, if tetraethoxysilane (TEOS) is employed as a precursor with a glycerol solvent, the glycerol can exchange with the ethoxy groups:

In principle, the presence and concentration of these chemical groups can change the precursor reactivity (i.e., gel time), modify the gel microstructure (surface area, pore size distribution, etc.), change the aging characteristics, or change nearly any other characteristic of the gel.

The use of a new solvent system can change a wide range of processing parameters including gel time, viscosity, aging conditions and drying shrinkage. Many of these properties such as gel times are difficult to measure on thin films. Although bulk and thin film properties may be different, it is often useful to perform a series of experiments on bulk samples (e.g. approximately 5 mm diameter by 30 mm long) to provide a better understanding of how changing solvent systems affects the nanoporous silica process.

Glycerol can react with TEOS and produce a dried gel with surprisingly different properties than that of an ethanol/TEOS gel. Unanticipated property changes in the glycerol/TEOS based gels generally include (at least on most formulations):

Lower density is achievable without supercritical drying or pre-drying surface modification

Greatly simplified aging

Shorter gel times even without a catalyst

Strengths of bulk samples which are approximately an order of magnitude greater (at a given density) than conventional TEOS gels

Very high surface area ((equivalent to)1,000 m2)/g)

High optical clarity of bulk samples (This is likely due to a narrow pore size distribution)

Low density -- With this invention, it is possible to form dried gels at very low densities without pre-drying surface modification or supercritical drying. These low densities can generally be down around .3 to .2 g/cm3) (non-porous SiO2)) has a density of 2.2 g/cm3)), or with care, below .1 g/cm3). Stated in terms of porosity (porosity is the percentage of a structure which is hollow), this denotes porosities of about 86% and 91% (about 95% porosity with a density of .1 g/cm3)). As shown in Figure 3, these porosities correspond to dielectric constants of about 1.4 for the 86% porous, and 1.2 for 91% porous. The actual mechanism that allows these high porosities is not fully known. However, it may be because the gels have high mechanical strength, because the gels do not have as many surface OH (hydroxyl) groups, a combination of these, or some other factors. This method also seems to obtain excellent uniformity across the wafer.

If desired, this process can be adjusted (by varying the TEOS/solvent ratios) to give any porosity from above 90% down to about 50%. Typical prior art dried gels with small pore sizes required either

supercritical drying or a surface modification step before drying to achieve these low densities. While some prior art xerogels have porosities greater than 50%; these prior art xerogels had substantially larger pore sizes (typically above 100 nm). These large pore size gels have significantly less mechanical strength. Additionally, their large size makes them unsuitable for filling small (typically less than 1 (mu) m) patterned gaps on a microcircuit. If desired, this process can also be adjusted (by varying the TEOS/solvent ratios) to provide porosities below 50%. Porosities down to 20% are possible when care is taken to prevent premature gelation.

Thus, this invention has enabled a new, simple nanoporous low density dielectric fabrication method. This new glycerol-based method allows both bulk and thin film aerogels to be made without supercritical drying, or a surface modification step before drying. Prior art aerogels have required at least one of these steps to prevent substantial pore collapse during drying. Density Prediction - By varying the ratio of glycerol to silicon (or other metal), the density after drying can be accurately predicted. This accuracy is likely due to the well controlled evaporation allowed by the low volatility glycerol solvent. As our process shows excellent shrinkage control during aging and drying, this allows accurate prediction of the density (and thus porosity) of the dried gel. Although density prediction had not generally been considered a large problem with bulk gels, it had typically been difficult to predict the final porosity of thin film gels. This accurate density prediction, even for low porosity dried gels, is one reason why this new process might be preferred over existing xerogel processes for forming low porosity gels.

Simplified Aging -- We have found that in the production of nanoporous dielectrics it is preferable to subject the wet gel thin film to a process known as aging. Hydrolysis and condensation reactions do not stop at the gel point, but continue to restructure, or age, the gel until the reactions are purposely halted. It is believed that during aging, preferential dissolution and redeposition of portions of the solid structure produce beneficial results. These beneficial results include higher strength, greater uniformity of pore size, and a greater ability to resist pore collapse during drying. However, aging a wet gel in thin film form is difficult, as the film contains an extremely small amount of pore fluid that should be held fairly constant for a period of time in order for aging to occur. If pore fluid evaporates from the film before aging has strengthened the network, the film will tend to densify in xerogel fashion. On the other hand, if excess pore fluid condenses from the atmosphere onto the thin film before the network has been strengthened, this may locally disrupt the aging process and cause film defects.

Our new, glycerol-based process has radically simplified aging of thin film nanoporous dielectrics. Other thin film nanoporous dielectric aging processes have either allowed significant evaporation, fluid condensation, or required a controlled aging atmosphere. During deposition and gelation, at least to some degree, these glycerol-based processes behave similarly to the ethylene glycol-based processes described below. However, the ethylene glycol-based gels typically require atmospheric controls to prevent significant evaporation during aging, even at room temperature. In contrast, the glycerol-based gels have dramatically lower evaporation and shrinkage rates during aging. This allows atmospheric control to be loosened or eliminated during aging. We can fabricate high quality, thin film, glycerol-based nanoporous dielectrics with only passive atmospheric controls during room temperature or high temperature aging.

Shorter Gel Times -- The use of glycerol also substantially shortens the gel time. Many typical ethanol-based precursors have gel times of at least 400 seconds, when catalyzed (much longer w/o catalysis). However, we discovered that some glycerol-based precursors will gel during wafer spin-on, even without catalysis. This quick gelation is not only faster than an ethanol-based gel, but also surprisingly faster than an ethylene glycol-based gel. Figure 4 shows gel times for two different ethylene glycol-based compositions as a function of the amount of ammonia catalyst used. These gel times are for bulk gels for which there is no evaporation of ethanol and/or water as there would be for thin films.

Evaporation increases the silica content and thus, decreases the gel time. Therefore, these gel times may be the upper limit for a given precursor/catalyst. The gel times reported in Figure 4 are approximately an order of magnitude shorter than conventional ethanol-based precursors. Gel times generally also exhibit a first order dependence on the concentration of ammonia catalyst. This implies that it may be possible to easily control the gel times.

For thin films of these new glycerol-based gels, it is routine to obtain gelation within seconds, even without a gelation catalyst. We have identified several mechanisms that can be used to launch gelation in thin films, without the addition of a catalyst. One method is the concentration of the precursor sol by allowing a volatile solvent to evaporate. Another method is increasing the pH by allowing an acid in the precursor sol to evaporate. This evaporative basification relies on increasing the precursor sol pH to help initiate gelation. However, this basification process does not typically require a pH change from below 7 to above 7. This evaporative basification acts similarly to a typical base catalysis process, greatly speeding gelation. At room temperature and pressure, some acids, such as nitric acid, have evaporation rates comparable to ethanol. Varying the concentrations and/or types of the high volatility solvent(s) and/or stabilizing acid provides a simple, yet tremendous flexible method for adjusting the gelation time.

Higher Strength -- The properties of the glycerol-based samples appear to be quite different from regular gels as evidenced by both their low degree of drying shrinkage and differences in qualitative handling of the wet and dry gels. Thus, upon physical inspection, the glycerol-based dried gels seem to have improved mechanical properties as compared to both conventional and ethylene glycol-based dried gels. Figure 5 shows the bulk modulus measured during isostatic compaction measurements of one sample prepared using one ethylene glycol-based and one conventional ethanol-based dried bulk gel (both have the same initial density). After initial changes attributed to buckling of the structure, both samples exhibit power law dependence of modulus with density. This power law dependence is usually observed in dried gels. However, what is surprising is the strength of the ethylene glycol-based dried gel. At a given density (and thus, dielectric constant), the modulus of this sample of the ethylene glycol dried gel is an order of magnitude higher than the conventional dried gel. Preliminary evaluations show that the glycerol-based gels are even stronger than the ethylene glycol-based gels. These evaluations include qualitative handling tests and information based on the shrinkage during drying. The reasons for this strength increase are not totally clear. However, preliminary experiments indicate that our rapid gelation times and/or narrow pore size distribution may be responsible for the high strengths.

High surface area -- We measured the surface areas of some dried bulk gels. These surface areas were on the order of 1,000 m2)/g, as compared to our typical ethanol-based dried gels which have surface areas in the 600-800 m2)/g range. These higher surface areas may imply smaller pore size and improved mechanical properties. It is unclear at this time why these higher surface areas are obtained with the glycerol-based dried gels.

Pore size distribution -- The optical clarity of these dried bulk gels was greater than any ethanol-based dried gels at this density that we have previously made. It is possible that this excellent optical clarity is due to a very narrow pore size distribution. However, it is unclear why the glycerol has this effect. Preliminary experiments show that one possible explanation is that rapid gelation times may be linked to a narrow pore size distribution. Figure 6 shows the pore size distribution (as measured by BJH nitrogen desorption measurements) of a bulk gel sample with a density of about .57 g/cm3). The mean pore diameter (desorption method) of this sample was 3.76 nm. As the typical pores are not truly cylindrical, diameter, as used herein, actually refers to the diameter of an equivalent cylinder with the same surface area to volume ratio as the overall gel's surface area to volume ratio.

As shown above, some properties of the glycerol-based gels apply to both bulk gels and thin films. However, some advantages are most evident when applied to thin films, such as nanoporous dielectric

films on semiconductor wafers. One important advantage is that this new method allows high quality nanoporous films to be processed with no atmospheric controls during deposition or gelation.

Although it is important to be able to deposit and gel thin nanoporous films without atmospheric controls, it is also desirable to age thin nanoporous films without atmospheric controls. It has been discovered that this can present a bigger challenge than deposition. The primary reason is that while deposition and room temperature gelation can take place in minutes, or even seconds; room temperature aging typically requires hours. Thus, an evaporation rate that provides acceptable shrinkage for a short process, may cause unacceptable shrinkage when the process times are lengthened by an order of magnitude.

As an example, we have found that with some glycerol-based gels, a satisfactory aging time at room temperature is on the order of a day. However, Table 1 shows that, by using higher temperatures, we can age thin films with times on the order of minutes. These aging times are comparable to the preferred aging time of many typical ethanol-based and ethylene glycol-based gels. Thus, when these times and temperatures are combined with the evaporation rates of Figure 1, Figure 7, and Figure 2, they give the approximate thickness loss during aging as shown in Table 2. These estimated thickness losses need to be compared with acceptable thickness losses, particularly for thin film applications. While no firm guidelines for acceptable thickness loss exist, one proposed guideline, for some microcircuit applications such as nanoporous dielectrics, is that the thickness losses should be less than 2% of the film thickness. For a hypothetical nominal film thickness of 1 (mu)m (Actual film thicknesses may typically vary from significantly less than .5 (mu)m to several (mu)m thick), this gives an allowable thickness loss of 20 nm. As shown in Table 2, the glycerol-based gels can achieve this preliminary goal without atmospheric control at room temperature. Thus, this invention allows controlled porosity thin film nanoporous aerogels to be deposited, gelled, aged, and dried without atmospheric controls. In another aspect, this invention allows controlled porosity thin film nanoporous aerogels to be deposited, gelled, rapidly aged at an elevated temperature, and dried with only passive atmospheric controls, such as limiting the volume of the aging chamber.

Improved yield and reliability considerations may require thickness losses below 2%, such as less than .5% or .1%. By using passive atmospheric control, this invention can be extended to these, and even lower evaporation losses. This passive control involves placing the gel in a relatively small closed container, at least during aging. In this aspect of the invention, evaporation from the wafer acts to raise the saturation ratio of the atmosphere inside the closed container. At any given temperature, this evaporation continues until the partial pressure of the vapor increases enough to equal the vapor pressure of the liquid. Thus, solvent/temperature combinations with lower vapor pressure will not allow as much liquid solvent to evaporate as a higher vapor pressure combination allows. Figure 8 shows how vapor pressure varies with temperature for several solvents. If the container size is known, the amount of evaporation can be calculated. Figure 9 shows an estimate of how thick of layer of solvent could potentially be evaporated if a 70% porous gel is placed in a 5 mm high cylindrical container that is the same diameter as the wafer. Figure 10 shows a similar estimate for a container with a 1 mm high airspace above the wafer. These figures show that, with a 5 mm high airspace, the 20 nm preliminary goal is feasible up to 120 degrees C for glycerol-based gels, but only up to 50 degrees C for ethylene glycol-based gels. With the 1 mm airspace, the 20 nm goal is feasible all the way up to 150 degrees C for the glycerol-based gels, but only up to 80 degrees C for the ethylene glycol-based gels. Of course, lower temperature processing allows less evaporation. Passive evaporation control using the 1 mm containers allows less than 1 nm of thickness loss (.1% of a 1(mu)m thick film) for the glycerol-based gels, even at 100 degrees C.

There are many variations on this passive control approach. One variation allows the container size to increase. The thickness loss will linearly increase with the container volume. However, even a 1000

cubic centimeter container typically allows only 5 nm of glycerol evaporation at 80 degrees C. Another variation is the gel porosity. Higher porosity gels generally experience greater thickness losses while lower porosity gels generally experience slightly smaller thickness losses.

One disadvantage of glycerol is its relatively high viscosity which can cause problems with gap-filling and/or planarization. As described above, a low viscosity, high volatility solvent can be used to lower the viscosity. Figure 11A shows the calculated viscosity of some ethanol/glycerol and methanol/glycerol mixtures at room temperature. As the figure shows, alcohol can significantly reduce the viscosity of these mixtures. Figure 11B shows the calculated viscosity of some ethanol/ethylene glycol and methanol/ethylene glycol mixtures at room temperature. As this figure shows, the ethylene glycol is much less viscous than the glycerol, and small quantities of alcohol significantly reduce the viscosity of these mixtures. Also, if the viscosity using ethanol in the stock solution is higher than desired, further improvement can be realized by employing methanol in the precursor solution. The viscosities reported in Figures 11A-11B are for pure fluid mixtures only. In fact, depending upon the film precursor solution, the precursor solution might contain glycerol, alcohol, water, acid and partially reacted metal alkoxides. Of course, the viscosity can be increased before deposition by catalyzing the condensation reaction and hence, the values reported in Figures 11A-11B represent lower bounds.

This multi-solvent approach may be combined with or replaced by an alternative approach. This alternate approach use elevated temperatures to reduce the sol viscosity during application. By heating and/or diluting the precursor during deposition, (such as by heating the transfer line and deposition nozzle of a wafer spin station) the viscosity of the precursor sol can be substantially lowered. Not only does this preheat lower the sol viscosity, it will also speed gel times and accelerate the evaporation of any high volatility solvents. It may also be desirable to preheat the wafer. This wafer preheat should improve process control and may improve gap fill, particularly for the more viscous precursors. However, for many applications, wafer preheat is not required, thus simplifying process flows. When using a spin-on application method with this no wafer preheat approach, the spin station would not require a temperature controlled spinner.

Dried gels produced with this simple thin film aerogel fabrication process can be used in many applications. Some of these uses may not have been cost effective using prior art methods. These uses include low dielectric constant thin films (particularly on semiconductor substrates), miniaturized chemical sensors, thermal isolation structures, and thermal isolation layers (including thermal isolation structures for infrared detectors). As a general rule, many low dielectric constant thin films prefer porosities greater than 60%, with critical applications preferring porosities greater than 80 or 90%, thus giving a substantial reduction in dielectric constant. However, structural strength and integrity considerations may limit the practical porosity to no more than 90%. Some applications, including thermal isolation structures and thermal isolation layers, may need to sacrifice some porosity for higher strength and stiffness. These higher stiffness requirements may require dielectrics with porosities as low as 30 or 45%. In other high strength/toughness applications, especially sensors, where surface area may be more important than density, it may be preferable to use a low porosity gel with a porosity between 20% and 40%.

The thin film discussion above has centered around thin film aerogels for microelectronic circuits. However, aerogels are also useful in other applications, such as thin films on passive substrates. These new high strength, easy to fabricate gels now make many of these uses practical. For purposes of this application, a passive substrate is defined as a substrate that does not comprise or contain a microelectronic circuit, or at least where there is no interaction between the aerogel and the electronics. Sol-Gel Science by C.J. Brinker and G.W. Scherer describes several of these uses in chapter 14. These passive uses may partially include some types of optical coatings, some types of protective coatings, and some types of porous coatings.

Antireflective (AR) coatings can require a wide range of porosities. These will typically range from 20% porous to 70% porous, although higher porosities (above 90%) may be useful where there is adequate surface protection, and lower porosities (down to 10%, or below) may be useful in high performance coatings or coatings on substrates with a high index of refraction. In some single layer AR coatings, it may be preferable to use gels with porosities between 30% and 55%. Higher performance, multi-layer AR coatings will prefer denser layers (e.g., porosity between 10% and 30%) next to the substrate, and less dense layers (e.g., porosity between 45% and 90%) next to the air interface. For higher strength/toughness applications, especially where high strength and surface area are the primary goals, it may be preferable to use a low porosity gel with a porosity between 20% to 40%. Other thin film coatings may need the lowest density practical, thus needing porosities greater than 85%, 90%, or even 95%.

There are also many bulk gel applications that can benefit from these new high strength, easy to fabricate aerogels. These bulk gel uses include (but are not limited to) nanoporous (e.g., molecular) sieves, thermal insulation, catalyst supports, adsorbents, acoustic insulation, and optiseparation membranes. As a general rule, many bulk uses prefer porosities greater than 60%, with critical applications preferring porosities greater than 80% or 90%. However, structural strength and integrity considerations may limit the practical porosity to no more than 95%. Some applications, possibly including sieves, may need to sacrifice some porosity for higher strength and stiffness. These higher stiffness requirements may require dielectrics with porosities as low as 30 or 45%. In other high strength/toughness applications, possibly including catalyst supports and sensors, where surface area may be more important than density, it may be preferable to use a low porosity gel with a porosity between 20% and 40%.

Typical sol-gel thin film processes produce gels which collapse and densify upon drying, thus forming xerogels having limited porosity (Up to 60% with large pore sizes, but generally substantially less than 50% with pore sizes of interest). Under the uncontrolled drying conditions of xerogel film formation, many of the internal pores permanently collapse. However, in thin film aerogel formation, the pores remain substantially uncollapsed, even though there may be a small amount of shrinkage during aging and/or drying that affects the final density.

Referring now to Figure 12A, a semiconductor substrate 10 (typically in wafer form) is shown. Common substrates include silicon, germanium, and gallium arsenide, and the substrate may include active devices, lower level wiring and insulation layers, and many other common structures not shown but known to those skilled in the art. Several patterned conductors 12 (e.g., of an Al-0.5%Cu composition) are shown on substrate 10. Conductors 12 typically run parallel for at least part of their length, such that they are separated by gaps 13 of a predetermined width (typically a fraction of a micron). Both the conductors and gaps may have height-to-width ratios much greater than shown, with larger ratios typically found in devices with smaller feature sizes.

In accordance with a first embodiment of the present invention, mix 61.0 mL tetraethoxysilane (TEOS), 61.0 mL glycerol, 4.87 mL water, and .2 mL 1M HNO3)) and reflux for 1.5 hours at (equivalent to) 60 (degree)C to form a stock solution. Equivalently, mix .27 mol TEOS, .84 mol glycerol, .27 mol water, and 2.04E-4 mol HNO3)) and reflux for 1.5 hours at (equivalent to) 60(degree)C. After the stock solution is allowed to cool, the solution may be diluted with ethanol to reduce the viscosity. One suitable stock solution: solvent volume ratio is 1:8. However, this ratio will depend upon desired film thickness, spin speed, and substrate. This is mixed vigorously and typically stored in a refrigerator at (equivalent to) 7(degree)C to maintain stability until use. The solution is typically warmed to room temperature prior to film deposition. 3-5 mL of this precursor sol may be dispensed at room temperature onto substrate 10, which is then spun at 1500 to 5000 rpm (depending on desired film thickness) for about 5-10 seconds to form sol thin film 14. The deposition can be performed in an atmosphere that has no

special control of solvent saturation (e.g., in a cleanroom with non-exotic humidity controls). During and after this deposition and spinning, the ethanol, water, and the nitric acid are evaporating from film 14, but due to glycerol's low volatility, no substantial evaporation of the glycerol is occurring. This evaporation temporarily cools the thin film, although the film temperature rises within seconds after the evaporation rate drops off. This cooling retards, but does not prevent gelation. This evaporation also shrinks thin film 14 and concentrates the silica content of the sol, forming reduced thickness film 18. Figure 12B shows a reduced thickness sol film 18 obtained after substantially all (about 95% or more) of the ethanol has been removed. This concentrating, evaporative basification, and/or rewarming of the film typically cause gelation within seconds.

Film 18 has an approximately known ratio of silicon to pore fluid at the gel point. This ratio is approximately equal to the ratio of TEOS to glycerol in the as-deposited sol (with minor changes due to remaining water, continued reactions and incidental evaporation). As this method largely prevents the gel from permanently collapsing, this ratio determines the density of the aerogel film that will be produced from the sol thin film.

After gelation, the thin film wet gel 18 comprises a porous solid and a pore fluid, and can preferably be allowed time to age at one or more controlled temperatures, e.g., about a day at room temperature. It should be noted that the pore fluid changes somewhat during processing. These changes may be due to continued reactions, evaporation/condensation, or chemical additions to the thin film. Aging may preferably be accomplished by letting the substrate and gel sit for approximately 24 hours at about 25 (degree) C or by heating it to 130-150(degree) C for about 1 minute in a closed container.

Aged film 18 may be dried without substantial densification by one of several methods, including supercritical fluid extraction. However, with these new glycerol-based gels, one alternative is to use a solvent exchange to replace the aging fluid with a drying fluid and then air dry the film 18 from this drying fluid. This drying method uses a solvent exchange to replace the aging fluid with a different fluid. Whether this fluid is identical to the aging fluid or not, the pore fluid that is present during drying is sometimes referred to as "drying fluid". If used, the solvent exchange replaces the aging fluid that is dominated by the glycerol and its associated high surface tension with a drying fluid that has a lower surface tension. This solvent exchange may be carried out as a one or two step process. In the two step process, the first step replaces the aging fluid with an intermediate by dispensing approximately 3-8 mL of ethanol at room temperature (or warmer) onto aged thin film 18, then spinning the wafer between approximately 50 and 500 rpm for about 5-10 seconds. It sometimes requires between 3 and 6 spin-on sequences to replace most of the aging fluid. The second step preferably replaces the intermediate fluid with a drying fluid such as heptane. This step preferably comprises dispensing approximately 3-8 mL of heptane at room temperature (or warmer) onto aged thin film 18, then spinning the wafer between approximately 50 and 500 rpm for about 5-10 seconds. It sometimes requires between 3 and 6 spin-on sequences to replace most of the intermediate fluid. This solvent exchange method allows us to remove nearly all the glycerol-containing fluid before drying. The drying fluid (heptane in this case) is finally allowed to evaporate from the wet gel 18, forming a dry nanoporous dielectric (dried gel). If the film can be satisfactorily dried from a liquid that is soluble with the aging fluid, the intermediate may not be required. In many cases, the wet gel can be dried directly from ethanol, or other suitable solvent.

This evaporation may be performed by exposing the wafer surface to an atmosphere that is not near saturated with the drying fluid. For example, the wafer could be in a substantially uncontrolled atmosphere, or a drying gas could be introduced into the atmosphere. To prevent boiling, drying should preferably start at a temperature somewhat below the boiling point of the drying fluid, such as room temperature. If a higher boiling point drying fluid, such as glycerol, is used (e.g., drying without solvent replacement), the starting drying temperature can be increased to a temperature near or equal to the aging temperature. As the thin film becomes predominately dry (typically within seconds), the

temperature should then be increased above the boiling point of both the aging fluid and the drying fluid. This method prevents destructive boiling, yet insures that all fluid is removed. Glycerol, as well as some other fluids, either decompose at approximately the same temperature as they boil, or decompose in lieu of boiling. With these fluids, particularly fluids like glycerol that can decompose into toxic substances, care should be taken not to overheat the evaporated fluid or the undried wafer. After drying, it is preferable to bake the nanoporous dielectric for a short time (such as 300(degree) for 15 to 60 minutes) to help remove any residual materials, such as organics, that are in or on the dielectric. The theoretical dielectric constant (before surface modification) of this embodiment is 1.3.

In order to reduce the dielectric constant, it is preferable to dehydroxylate (anneal) the dried gel. This may be done by placing the wafer in a dry atmosphere with an agent, such as hexamethyldisilazane (HMDS) or hexaphenyldisilazane vapor. The HMDS will replace much of the water and/or hydroxyls bound to the dried gel's pore surfaces with methyl groups. This replacement may be performed at room temperature, or warmer. This replacement can not only remove water and/or hydroxyls, it can also render the dried gel hydrophobic (water repelling). The hexaphenyldisilazane will also remove water and/or hydroxyls and render the dried gel hydrophobic. However, the phenyl groups have a higher temperature stability than the methyl groups, at the expense of a slightly higher dielectric constant.

Figure 13 contains a flow chart of a general method for obtaining an aerogel thin film from a precursor sol according to one embodiment of the present invention. Table 3 is a quick summary of some of the substances used in this method.

In accordance with a second, higher density, embodiment of the present invention, mix 150.0 mL TEOS, 61.0 mL glycerol, 150.0 mL ethanol, 12.1 mL water, and .48 mL 1M HNO3)) and reflux for 1.5 hours at (equivalent to) 60(degree)C to form a stock solution. Equivalently, mix .67 mol TEOS, .84 mol glycerol, 2.57 mol ethanol, .67 mol water, and 4.90E-4 mol HNO3)) and reflux for 1.5 hours at (equivalent to) 60 (degree)C. After the stock solution is allowed to cool, the solution may be diluted with ethanol to reduce the viscosity. One suitable stock solution:solvent volume ratio is 1:8. This is mixed vigorously and typically stored in a refrigerator at (equivalent to) 7(degree)C to maintain stability until use. The solution is warmed to room temperature prior to film deposition. 3-5 mL of this precursor sol may be dispensed at room temperature onto substrate 10, which is then spun at 1500 to 5000 rpm (depending on desired film thickness) for about 5-10 seconds to form sol thin film 14. The deposition can be performed in an atmosphere that is not solvent controlled (e.g., standard exhausts in a cleanroom with non-exotic humidity controls). During and after this deposition and spinning, ethanol (a viscosity reduction additive and a reaction product from the TEOS and water) and water is evaporating from film 14, but due to glycerol's low volatility, no substantial evaporation of the glycerol is occurring. This evaporation shrinks thin film 14 and concentrates the silica content of the sol forming reduced thickness film 18. Figure 12B shows a reduced thickness sol film 18 obtained after substantially all (about 95% or more) of the water has been removed. This concentrating typically causes gelation within minutes.

Further processing generally follows the process described in the first embodiment. After gelation, the thin film wet gel 18 comprises a porous solid and a pore fluid, and can preferably be allowed time to age at one or more controlled temperatures. Aged film 18 may be dried without substantial densification by one of several methods, including supercritical fluid extraction. However, with the lower density formulations of these new glycerol-based gels, it is preferable to perform a non-supercritical drying, such as a solvent exchange followed by air drying the film 18 from the drying fluid, as described in the first embodiment. The nanoporous dielectric can then be subjected to a post-dry bake and/or a surface modification, as described in the first embodiment. The theoretical dielectric constant (before surface modification) of this embodiment is 1.6.

In accordance with a third, higher density, embodiment of the present invention, mix 208.0 mL TEOS,

61.0 mL glycerol, 208.0 mL ethanol, 16.8 mL water, and .67 mL 1M HNO_3)) and reflux for 1.5 hours at (equivalent to) 60(degree)C to form a stock solution. Equivalently, mix .93 mol TEOS, .84 mol glycerol, 3.56 mol ethanol, .93 mol water, and 6.80E-4 mol HNO_3)) and reflux for 1.5 hours at (equivalent to) 60 (degree)C. After the stock solution is allowed to cool, the solution may be diluted with ethanol to reduce the viscosity. One suitable stock solution:solvent volume ratio is 1:8. This is mixed vigorously and typically stored in a refrigerator at (equivalent to) 7(degree)C to maintain stability until use. The solution is warmed to room temperature prior to film deposition. 3-5 mL of this precursor sol may be dispensed at room temperature onto substrate 10, which is then spun at 1500 to 5000 rpm (depending on desired film thickness) for about 5-10 seconds to form sol thin film 14. The deposition can be performed in an atmosphere that is not solvent controlled (e.g., standard exhausts in a cleanroom with non-exotic humidity controls). During and after this deposition and spinning, ethanol and water is evaporating from film 14, but due to glycerol's low volatility, no substantial evaporation of the glycerol is occurring. This evaporation shrinks thin film 14 and concentrates the silica content of the sol forming reduced thickness film 18. Figure 12B shows a reduced thickness sol film 18 obtained after substantially all (about 95% or more) of the water has been removed. This concentrating typically causes gelation within minutes.

Further processing generally follows the process described in the first embodiment. After gelation, the thin film wet gel 18 comprises a porous solid and a pore fluid, and can preferably be allowed time to age at one or more controlled temperatures. Aging may be accomplished by letting the device sit for approximately 24 hours at 25(degree) C. Aged film 18 may be dried without substantial densification by one of several methods, including supercritical fluid extraction, or a solvent exchange followed by air drying. However, especially in this higher density formulation of these new glycerol-based gels, it is preferable to air dry the film 18 from the aging fluid. In this direct drying method, the wafer surface is exposed to an atmosphere that is not near saturated with the drying fluid. A simple method is to remove the cover from a low volume aging chamber, thus exposing the gel surface to a substantially uncontrolled atmosphere. Another method introduces a drying gas into the aging chamber or atmosphere. With this direct drying method, the starting drying temperature can preferably be increased to a temperature near or equal to the aging temperature. This high temperature drying reduces surface tension and associated shrinkage, speeds drying, and simplifies processing. As the thin film becomes predominately dry (typically within seconds for high temperature drying), the temperature should then be increased above the boiling point of both the aging fluid and the drying fluid (they are often the same fluid). This method prevents destructive boiling, yet insures that all fluid is removed. Since this method's drying fluid comprises glycerol, which can decompose into toxic substances, care should be taken not to overheat the evaporated fluid or the undried wafer. The nanoporous dielectric can then be subjected to a post-dry bake and/or a surface modification, as described in the first embodiment. The theoretical dielectric constant (before surface modification) of this embodiment is 1.76.

In accordance with a fourth embodiment of the present invention, mix 278.0 mL TEOS, 61.0 mL glycerol, 278.0 mL ethanol, 22.5 mL water, and .90 mL 1M HNO_3)) and reflux for 1.5 hours at (equivalent to) 60(degree)C to form a stock solution. Equivalently, mix 1.25 mol TEOS, .84 mol glycerol, 4.76 mol ethanol, 1.25 mol water, and 9.1E-4 mol HNO_3)) and reflux for 1.5 hours at (equivalent to) 60(degree)C. After the stock solution is allowed to cool, the solution may be diluted with ethanol to reduce the viscosity. One suitable stock solution:solvent volume ratio is 1:8. This is mixed vigorously and typically stored in a refrigerator at (equivalent to) 7(degree)C to maintain stability until use. The solution is warmed to room temperature prior to film deposition. 3-5 mL of this precursor sol may be dispensed at room temperature onto substrate 10, which is then spun at 1500 to 5000 rpm (depending on desired film thickness) for about 5-10 seconds to form sol thin film 14. The deposition can be performed in an atmosphere that is not solvent controlled (e.g., standard exhausts in a cleanroom with non-exotic humidity controls). During and after this deposition and spinning, ethanol and water is evaporating from film 14, but due to glycerol's low volatility, no substantial evaporation of the glycerol is occurring. This evaporation shrinks thin film 14 and concentrates the silica content of the sol forming

reduced thickness film 18. Figure 12B shows a reduced thickness sol film 18 obtained after substantially all (about 95% or more) of the water has been removed. This concentrating typically causes gelation within minutes.

Further processing generally follows the process described in the third embodiment. After gelation, the thin film wet gel 18 comprises a porous solid and a pore fluid, and can preferably be allowed time to age at one or more controlled temperatures. Aged film 18 may be dried without substantial densification by one of several methods, including supercritical fluid extraction. However, it is preferable to air dry the film 18 from the aging fluid, as described in the third embodiment. The nanoporous dielectric can then be subjected to a post-dry bake and/or a surface modification, as described in the first embodiment. The theoretical dielectric constant (before surface modification) of this embodiment is 1.96.

In accordance with a fifth embodiment of the present invention, mix 609.0 mL TEOS, 61.0 mL glycerol, 609.0 mL ethanol, 49.2 mL water, and 1.97 mL 1M HNO3)) and reflux for 1.5 hours at (equivalent to) 60(degree)C to form a stock solution. Equivalently, mix 2.73 mol TEOS, .84 mol glycerol, 10.4 mol ethanol, 2.73 mol water, and 2.00E-3 mol HNO3)) and reflux for 1.5 hours at (equivalent to) 60(degree) C. After the stock solution is allowed to cool, the solution may be diluted with ethanol to reduce the viscosity. One suitable stock solution:solvent volume ratio is 1:8. This is mixed vigorously and typically stored in a refrigerator at (equivalent to) 7(degree)C to maintain stability until use. The solution is warmed to room temperature prior to film deposition. 3-5 mL of this precursor sol may be dispensed at room temperature onto substrate 10, which is then spun at 1500 to 5000 rpm (depending on desired film thickness) for about 5-10 seconds to form sol thin film 14. The deposition can be performed in an atmosphere that is not solvent controlled (e.g., standard exhausts in a cleanroom with non-exotic humidity controls). During and after this deposition and spinning, ethanol and water is evaporating from film 14, but due to glycerol's low volatility, no substantial evaporation of the glycerol is occurring. This evaporation shrinks thin film 14 and concentrates the silica content of the sol forming reduced thickness film 18. Figure 12B shows a reduced thickness sol film 18 obtained after substantially all (about 95% or more) of the water has been removed. This concentrating typically causes gelation within minutes.

Further processing generally follows the process described in the third embodiment. After gelation, the thin film wet gel 18 comprises a porous solid and a pore fluid, and can preferably be allowed time to age at one or more controlled temperatures. Aged film 18 may be dried without substantial densification by one of several methods, including supercritical fluid extraction. However, it is preferable to air dry the film 18 from the aging fluid, as described in the third embodiment. The nanoporous dielectric can then be subjected to a post-dry bake and/or a surface modification, as described in the first embodiment. The theoretical dielectric constant (before surface modification) of this embodiment is 2.5.

Other ratios of solvent to reactant ratios can be used to provide different porosities/dielectric constants. Figure 14 shows the theoretical relationship between the molar ratio of glycerol molecules to metal atoms and the porosity of a nanoporous dielectric for the case where all ethanol is evaporated from the deposited sol. Typically, the higher porosity glycerol-based gels (generally less than about .51 g/cc) prefer a solvent exchange or other method to lessen shrinkage during drying. On the other hand, the lower porosity gels require care to prevent early gelation. This may comprise pH adjustment, temperature control, or other methods known in the art. In some applications, it is also permissible to allow high volatility solvent evaporation after gelation.

As described above, the higher density glycerol-based gels (generally greater than about .64 g/cc) can be aged and dried with little shrinkage, even without a solvent exchange. An unaged wafer may be placed in a small volume furnace, or a small container, which can go on a hot plate. After an optional evacuation, the container is sealed at room temperature. The container remains sealed as the temperature is ramped up, quickly aging the film, and lowering the aging/drying fluid viscosity. After sufficient

aging (possibly during the temperature ramp), the gel is ready for drying. At temperatures near glycerol's boiling point, the glycerol viscosity can be low enough (compared to the strength of an aged film of the predetermined porosity), that the glycerol in the furnace atmosphere can be removed and the film directly dried. Note that, in the most demanding low density applications, a somewhat lower surface tension can be obtained by increasing the drying temperature above the boiling point of glycerol. In these cases, the furnace needs to withstand the pressure (most sub-critical drying situations can be handled with pressures under 1 to 3 MPa). Additionally, care needs to be taken that the glycerol in the furnace atmosphere is, especially at first, slowly removed. The glycerol in the furnace atmosphere may be removed, e.g., by bleeding off the pressure, by a vacuum pump, or by sweeping the glycerol off with a gas. The furnace temperature may be held constant or continue to be raised while the glycerol is being removed (the furnace may be ramped on up to the bake temperature while sweeping the glycerol off with the gas). While some glycerol can be introduced during heating to minimize evaporation from the film, preferably the furnace volume is low enough that evaporation does not significantly reduce film thickness even without the introduction of glycerol during heating. If a film requires supercritical drying, perhaps to eliminate even temporary shrinkage, it is preferable to use a CO2)) solvent exchange as is well known in the art.

Although the same stock solutions can be used for bulk aerogels as thin film aerogels, the processing is substantially different. With different stock solution mixtures, the following example can be adapted to provide bulk gels with different porosities. In accordance with a bulk aerogel embodiment of the present invention, mix 208.0 mL TEOS, 61.0 mL glycerol, 208.0 mL ethanol, 16.8 mL water, and .67 mL 1M HNO3)) and reflux for 1.5 hours at (equivalent to) 60(degree)C to form a stock solution. Equivalently, mix .93 mol TEOS, .84 mol glycerol, 3.56 mol ethanol, .93 mol water, and 6.80E-4 mol HNO3)) and reflux for 1.5 hours at (equivalent to) 60(degree)C. This is typically stored in a refrigerator at (equivalent to) 7(degree)C to maintain stability until use. The stock solution is preferably warmed to room temperature prior to placing into molds. After pouring into molds, the ethanol, water, and acid is allowed to evaporate, but due to glycerol's low volatility, no substantial evaporation of the glycerol is occurring. This evaporation reduces the volume of the stock solution precursor sol and concentrates the silica content of the sol. It is allowable for at least some of the evaporation to occur before filling the mold. This pre-fill evaporation might be especially useful if the configuration of the mold does not lend itself to substantial evaporation after filling, such as a low exposed surface area mold or a mold configuration that is incompatible with shrinkage. Although this evaporation is not required, it has several advantages, including faster gelation without a catalyst and less shrinkage after gelation.

After this evaporation, the sol has an approximately known ratio of silicon to pore fluid at the gel point. This ratio is approximately equal to the ratio of TEOS to glycerol in the precursor mix (with minor changes due to remaining water, continued reactions and incidental evaporation). As this method largely prevents the gel from permanently collapsing, this ratio determines the density of the aerogel that will be produced. If the sol does not gel during evaporation, this sol will gel soon after substantially all of the water, ethanol, and acid has evaporated.

Alternatively, one may catalyze the precursor with .5M ammonium nitrate before filling the mold. With this mixture, the sol typically gels in minutes. Remove the wet gel from the mold and allow the ethanol and water to evaporate. Typically, the gel will shrink during this evaporation. However, as with the other approaches, when the evaporation is substantially complete, the sol has an approximately known ratio of silicon to pore fluid at the gel point. This ratio is approximately equal to the ratio of TEOS to glycerol in the precursor mix (with minor changes due to remaining water, continued reactions and incidental evaporation). As this method largely prevents the gel from permanently collapsing, this ratio determines the density of the aerogel that will be produced.

After gelation, the wet gel comprises a porous solid and a pore fluid, and can preferably be allowed time

to age at one or more controlled temperatures. Aging may preferably be accomplished by letting the substrate and gel sit for approximately 24 hours at about 25(degree) C or by heating it to 130-150 (degree) C for about 5 minutes in a closed container. These high temperature aging parameters are valid for a 5 mm diameter bulk aerogel. However, due to the wet gel's low thermal conductivity, the high temperature accelerated aging time and temperature combinations are highly dependent upon the configuration of the bulk gel.

After this initial aging, remove the gel from the molds and dry directly from the mother liquor (that is, the pore fluid remaining at the end of aging, with no solvent exchanges for aging or drying). A slow ramp to and hold at about 500(degree) C will dry the gel.

Instead of drying directly from the mother liquor, it may be preferable, particularly with higher porosity gels, to perform a solvent exchange. This solvent exchange may be carried out as a one or two step process. The first step replaces the aging fluid with an intermediate and the second step preferably replaces the intermediate fluid with a low surface tension drying fluid such as heptane. In this method, It is preferable to remove the gels from the molds and place it in sealed tubes containing ethanol and allow a pore fluid exchange for 8 hours at 50 degrees C. At the end of a 8 hour interval, rinse the gels with ethanol and then store in fresh ethanol in an oven at 50 degrees C. After three to six such intervals, replace the ethanol with hexane in a similar manner. This solvent exchange method allows us to remove nearly all the glycerol-containing fluid before drying. The drying fluid (heptane in this case) is finally allowed to evaporate from the wet gel, forming a dry aerogel. If the film can be satisfactorily dried from a liquid that is soluble with the aging fluid, the intermediate may not be required. In many cases, the wet gel can be dried directly from ethanol, or other suitable solvent.

After drying, it is often preferable to bake the aerogel for a short time (such as 300(degree) for 15 to 60 minutes) to help remove any residual materials, such as organics, that are in or on the aerogel. In some applications, it is also desirable to dehydroxylate (anneal) the dried gel. This may be done by placing the dry aerogel in a dry atmosphere comprising a surface modification agent, such as trimethylchlorosilane (TMCS), hexamethyldisilazane (HMDS), or hexaphenyldisilazane vapor. The HMDS will replace much of the water and/or hydroxyls bound to the dried gel's pore surfaces with methyl groups. This replacement can be performed at room temperature, or warmer. This replacement can not only remove water and/or hydroxyls, it can also render the dried gel hydrophobic (water repelling). The hexaphenyldisilazane will also remove water and/or hydroxyls and render the dried gel hydrophobic. However, the phenyl groups have a higher temperature stability than the methyl groups.

In accordance with an ethylene glycol-based embodiment of the present invention, mix tetraethoxysilane (TEOS), ethylene glycol, ethanol, water, and acid (1M HNO3))) in a molar ratio of 1 : 2.4 : 1.5 : 1 : 0.042 and reflux for 1.5 hours at (equivalent to) 60(degree)C. After the mixture is allowed to cool, the solution is diluted down with ethanol to a composition of 70% (by volume) original stock solution and 30% (by volume) ethanol. This is mixed vigorously and typically stored in a refrigerator at (equivalent to) 7(degree)C to maintain stability until use. The solution is warmed to room temperature prior to film deposition. A mixture of stock solution and 0.25M NH4))OH catalyst (10:1 volume ratio) is combined and mixed. 3-5 mL of this precursor sol may be dispensed at room temperature onto substrate 10, which is then spun at 1500 to 5000 rpm (depending on desired film thickness) for about 5-10 seconds to form sol thin film 14. The deposition can be performed in an atmosphere that is uncontrolled. However, it is preferable to deposit and gel the sol in a clean room with standard humidity controls. During and after this deposition and spinning, the ethanol/water mixture is evaporating from film 14, but due to ethylene glycol's low volatility, no substantial evaporation of the ethylene glycol is occurring. This evaporation shrinks thin film 14 and concentrates the silica content of the sol forming reduced thickness film 18. Figure 12B shows a reduced thickness sol film 18 obtained after substantially all (about 95% or more) of the ethanol has been removed. This concentrating, combined with the catalyst, typically causes gelation

within minutes or seconds.

Film 18 has an approximately known ratio of silicon to pore fluid at the gel point. This ratio is approximately equal to the ratio of TEOS to ethylene glycol in the as-deposited sol (with minor changes due to remaining water, continued reactions and incidental evaporation). To the extent that the gel is prevented from collapsing, this ratio will determine the density of the aerogel film that will be produced from the sol thin film.

After gelation, the thin film wet gel 18 comprises a porous solid and a pore fluid, and can preferably be allowed time to age at one or more controlled temperatures, e.g., about a day at room temperature. It should be noted that the pore fluid changes somewhat during processing. These changes may be due to continued reactions and/or evaporation/condensation. Aging may preferably be accomplished by letting the device sit in a low volume aging chamber for approximately 5 minutes at about 100 degrees C.

Aged film 18 may be dried without substantial densification by one of several methods, including supercritical fluid extraction, or a solvent exchange followed by air drying. However, it is preferable to air dry the film 18 from the aging fluid, as described in the third glycerol embodiment. The nanoporous dielectric can then be subjected to a post-dry bake and/or a surface modification, as described in the first glycerol embodiment.

In accordance with another ethylene glycol-based embodiment of the present invention, mix tetraethoxysilane (TEOS), ethylene glycol, water, and acid (1M HNO3))) in a molar ratio of 1 : 4 : 1 : 0.042 and reflux for 1.5 hours at (equivalent to) 60(degree)C. This is typically stored in a refrigerator at (equivalent to) 7(degree)C to maintain stability until use. The solution is preferably warmed to room temperature prior to film deposition. 3-5 mL of this precursor sol may be dispensed (without catalyst) at room temperature onto substrate 10, which is then spun at 1500 to 5000 rpm (depending on desired film thickness) for about 5-10 seconds to form sol thin film 14. The deposition can be performed in an atmosphere that is uncontrolled. However, it is preferable to deposit and gel the sol in a clean room with standard humidity controls. During and after this deposition and spinning, ethanol and water is evaporating from film 14, but due to ethylene glycol's low volatility, no substantial evaporation of the ethylene glycol is occurring. This evaporation shrinks thin film 14 and concentrates the silica content of the sol forming reduced thickness film 18. Figure 12B shows a reduced thickness sol film 18 obtained after substantially all (about 95% or more) of the water has been removed. This concentrating typically causes gelation within minutes.

After gelation, the thin film wet gel 18 comprises a porous solid and a pore fluid, and can preferably be allowed time to age at one or more controlled temperatures, e.g., about a day at room temperature. It should be noted that the pore fluid changes somewhat during processing. Aging may preferably be accomplished by letting the device sit in a low volume aging chamber for approximately 5 minutes at about 100 degrees C.

Aged film 18 may be dried without substantial densification by one of several methods, including supercritical fluid extraction, or a solvent exchange followed by air drying. However, it is preferable to air dry the film 18 from the aging fluid, as described in the third glycerol embodiment. The nanoporous dielectric can then be subjected to a post-dry bake and/or a surface modification, as described in the first glycerol embodiment.

The discussion to this point has shown some of the advantages of aging in a closed container. Since suitable aging chambers do not seem to exist, we will describe the chambers we have invented to implement this process. One embodiment of aging container is illustrated in Figures 16A, 16B and 16C.

In this embodiment, a processing apparatus comprises a body 20, having a substantially planar plate 22 with a resilient seal 24 attached thereto. Plate 22 need only be planar to the extent necessary to provide clearance with a thin film during operation, and may be constructed of any material compatible with the underlying process (e.g., semiconductor fabrication), although materials with high thermal conductivity, such as stainless steel, glass, or aluminum are preferred. Resilient seal 24 should preferably be designed to withstand wet gel processing temperatures and pore fluids; many suitable materials, including TEFLON- and neoprene-based materials, are known to those of ordinary skill in the art. Depending on the nature of temperature control used in the apparatus, it may be preferable to have seal 24 be either substantially thermally insulating or thermally conductive.

In operation, body 20 may simply be rested on a substrate 26, as shown in Figure 16C. This substrate may be an optical substrate, such as glass or plastic, or a semiconductor substrate, such as a Si wafer. In this embodiment, seal 24 functions both as an atmospheric seal and as a spacer which sets the volume of chamber 32 formed by substrate surface 28, chamber surface 30 and seal 24. For example, seal 24 may be designed to compress to a thickness of about 1 mm under the weight of plate 22, thus creating chamber 32 with a 1 mm height when body 20 is placed on substrate 26. For many thin film applications, chamber 32 need only be substantially sealed, as some small degree of vapor leakage over the course of processing substrate 26 will not appreciably affect the final film properties.

Body 20 finds application at many points in an aerogel thin film process. It may be used to limit evaporation before a sol film has gelled, as an aging chamber for wet gel thin films, as a storage or transport chamber for such films, or as a drying chamber. In all of these applications, it is recognized that both sol and gel thin films contain extremely small amounts of liquid, such that a chamber of limited volume is necessary to prevent substantial evaporation from the film.

In another embodiment, body 20 may comprise more elements, as shown in Figures 17A and 17B. In this embodiment, body 20 additionally comprises a substrate holder 36 and substrate temperature control means 34. This embodiment shows the additional aspect of a seal 24 located outboard of the substrate (or in some cases seal 24 may even be deleted), such that a thin film may be formed on the entirety of substrate surface 28. When chamber 32 is closed, planar plate 22 and wafer holder 36 may be thermally coupled such that temperature control means 34 may be used to simultaneously regulate the temperature of body 20, substrate 26 and chamber 32.

In another embodiment shown in Figures 18A and 18B, seal 24 provides some degree of thermal isolation between planar plate 22 and wafer holder 36. This allows temperature control means 34 to control substrate temperature, while separate temperature control means 38 are used to control planar plate temperature. Such an embodiment may have an advantage for drying a wet gel film, as the temperature of planar plate 22 can be selectively lowered to promote condensation on chamber surface 30.

Figures 19A, 19B and 19C show additional aspects of these aging chambers. For example, in Figure 19A, substrate 26 is shown being processed in an inverted position. In this embodiment, accidental or purposeful condensation onto chamber surface 30 may be collected without the possibility of such condensation dropping onto substrate surface 26. In Figure 19B, not only is substrate 26 processed inverted, but a first solvent layer 42 (preferably of the same composition as at least one pore fluid) is dispensed, e.g., from a first solvent supply tube 40, onto chamber surface 30 prior to closing the chamber. In this embodiment, layer 42 may be used to help saturate the processing atmosphere, resulting in less evaporation of pore fluid from substrate 26.

In Figure 19C, an embodiment is shown wherein some atmospheric adjustment means 44 is connected through at least one port 46 (which may be closeable) to chamber 32. Atmospheric adjustment means 44

may be used to create a vacuum or to overpressure chamber 32 as appropriate, or to exchange the atmosphere in chamber 32, or to supply a pore fluid vapor to chamber 32. This embodiment may be used, for example, to age a thin film at a temperature higher than the boiling point of a pore fluid, by operating chamber 32 at above atmospheric pressure. This embodiment may also be used to remove at least a portion of the pore fluid vapor from chamber 32 after aging, thereby allowing the thin film to dry.

Although this invention has been described in terms of several embodiments, many of these steps may be modified within the scope of the invention, and other steps can be included to enhance the overall process. For example, the initial thin film may be deposited by other common methods, such as dip-coating, flow coating, or spray-coating instead of spin-coating. Likewise, the solvent exchange may use dip coating, spray coating, or immersion in a liquid or vaporous solvent instead of spin-coating. When using a vaporous solvent, the wafer may be cooled to a temperature lower than the atmosphere, thus promoting condensation on the wafer. While water might otherwise be considered a solvent in such a process, for discussion purposes in this application, water is not considered a solvent.

Although both glycerol and ethylene glycol each have unique advantages, there are other low volatility solvents that can be useful in low shrinkage nanoporous dielectric fabrication. Although it is preferable to analyze a solvent to determine its expected evaporation rate, a preliminary preference on the selection of the low volatility solvent can be made. Nearly all solvents that have a low evaporation rate at room temperature will have a boiling point greater than 140(degree) C. Although some solvents with boiling points less than 140(degree) C may be useful, a preferred evaporation rate will typically be found with solvents that have a boiling point greater than 160(degree) C, and more preferably greater than 190 (degree) C. Solvents with boiling points greater than 230(degree) C may also have low enough evaporation rates to be suitable for deposition and/or aging with little atmospheric control for short periods of time at 40-80(degree) C. For processing at 100-150(degree) C with little atmospheric control, it is preferable to use solvents with boiling points greater than 270(degree) C. This gives some rough preferences on the lower limit of preferred boiling points. There are also rough preferences on the upper limit of preferred boiling points. Most solvents with boiling points greater than 500(degree) C will be so viscous that they require extra care during processing. Typically, the more useful solvents will have boiling points less than 350(degree) C, and preferably less than 300(degree) C. If it is not convenient to dilute or heat the sol during deposition, it may even be preferable to use a low volatility solvent with a boiling point less than 250(degree) C. If no one solvent gives all the desired properties, two or more may be mixed to improve the performance. Thus, our initial preliminary preference on the selection of the low volatility solvent is a boiling point in the 175-250(degree) C range and (for TEOS based gels) that it be miscible with both water and ethanol. Based on these preliminary preferences, some suitable low volatility solvent candidates besides glycerol and ethylene glycol are 1,4-butylene glycol and 1,5-pentanediol.

If it is convenient to do the deposition and aging above room temperature, this opens up additional possibilities. One modification would be to use a solvent that is not a liquid, but a solid, at room temperature. This allows the potential use of many more materials. Many of these higher melting point materials have even lower volatility than the low volatility "room temperature liquid solvents" (liquid solvents) have at elevated deposition and aging temperatures. Although there is no required upper melting point temperature, process simplicity indicates that these "room temperature solid solvents" (solid solvents) should have melting points less than 60 degrees C, and preferably less than 40 degrees C. An additional desirable feature for a potential solid solvent is that it readily solidify to an amorphous phase. This amorphous solidification would reduce the chance of gel damage during an accidental cooling. Additionally, this might allow the solvent to be removed by freeze drying. An alternative approach to maintaining the precursor temperature above the melting point of a solid solvent is to dissolve the solid solvent in a carrier liquid. This carrier liquid can be water, alcohol, or any other liquid typically used in thin film aerogel/xerogel processing. The carrier liquid could also be a

compatible liquid introduced only as a carrier.

The surprisingly good behavior of glycerol and ethylene glycol give some clues to other preferred solvents. We have identified several solvents that may give properties slightly different than either ethylene glycol or glycerol, yet still retain many of their advantages. The most promising additional solvents include 1,2,4-butanetriol; 1,2,3- butanetriol; 2 methyl-propanetriol; and 2-(hydroxymethyl)-1,3-propanediol; 1-4, 1-4, butanediol; and 2-methyl-1,3-propanediol. Other potential solvents include the polyols, either alone or in combination with ethylene glycol, glycerol, or other solvents.

This use of a low volatility solvent allows a loosening of the required atmospheric control during deposition, gelation, and/or aging. This is because, that even though saturation should still preferably be avoided, the atmospheric solvent concentration can be lowered without excessive evaporation. This wider concentration window can be used to allow wider variations in temperature across the deposition chamber (especially near the wafer and any evaporative cooling effects). An initial goal is to allow at least a 1 degree C temperature variation. Thus, the vapor concentration of the low volatility solvent in the atmosphere should be such that the condensation temperature (analogous to dew point) of the solvent vapor is at least 1 degrees Celsius less than the temperature of the substrate. Actually, the critical item is the surface of the deposited sol and/or gelled sol. However, the thin film nature of the sol keeps the temperature differences between the sol and the substrate small. Since it is may be much easier to measure the substrate temperature, these two temperatures will be used interchangeably in this patent. Even though 1 degree C temperature uniformity may be obtainable under some conditions, volume production will probably require at least a 3 degree C tolerance window, and preferably a 10 degree C tolerance window. However, the ultimate goal is to deposit, gel, and age in an uncontrolled or a substantially uncontrolled atmosphere. In this most preferred approach (a substantially uncontrolled atmosphere), atmospheric controls during deposition, gelation, and aging are limited to standard cleanroom temperature and humidity controls, although the wafer and/or precursor sol may have independent temperature controls. If this substantially uncontrolled atmosphere allows excessive evaporation, then either passive or less preferably, active atmospheric controls may be needed. For the purposes of this application, passive controls are limited to the placing the wafer in a relatively small container. This container may be partially or fully sealed and may or may not also contain a liquid reservoir of the solvent. However, the container will not have exotic environmental controls for the wafer, container atmosphere, and/or reservoir.

Another example of modification to the basic method is that, before drying (and generally, but not necessarily, after aging), the thin film wet gel 18 may have its pore surfaces modified with a surface modification agent. This surface modification step replaces a substantial number of the molecules on the pore walls with those of another species. If a surface modifier is applied, it is generally preferable to remove the water from the wet gel 18 before the surface modifier is added. The water can be removed by rinsing the wafer in pure ethanol, preferably by a low speed spin coating as described in the solvent exchange in the first embodiment example. This water removal is beneficial, because water will react with many surface modification agents, such as HMDS; however, it is not necessary. With our new glycerol-based method, surface modification need not be performed to help prevent pore collapse, but it can be used to impart other desirable properties to the dried gel. Some examples of potentially desirable properties are hydrophobicity, reduced dielectric constant, increased resistance to certain chemicals, and improved temperature stability. Some potential surface modifiers that may impart desirable properties include hexamethyldisilazane (HMDS), the alkyl chlorosilanes (trimethylchlorosilane (TMCS), dimethyldichlorosilane, etc.), the alkylalkoxysilanes (trimethylmethoxysilane, dimethyldimethoxysilane, etc.), phenyl compounds and fluorocarbon compounds. One useful phenyl compound is hexaphenyldisilazane. Some other useful phenyl compounds will typically follow the basic formula, Phx))Ay))SiB(4-x-y))) , where, Ph is a phenolic group, A is a reactive group such as Cl or OCH3)), and B are the remaining ligands which, if there are two, can be the same group or different. Some examples

of these phenyl surface modification agents include compounds with 1 phenolic group such as phenyltrichlorosilane, phenyltrifluorosilane, phenyltrimethoxysilane, phenyltriethoxysilane, phenylmethylchlorosilane, phenylethyldichlorosilane, phenyldimethylethoxysilane, phenyldimethylchlorosilane, phenyldichlorosilane, phenyl(3-chloropropyl)dichlorosilane, phenylmethylvinylchlorosilane, phenethyldimethylchlorosilane, phenyltrichlorosilane, phenyltrimethoxysilane, phenyltris(trimethylsiloxy)silane, and phenylallyldichlorosilane. Other examples of these phenyl surface modification agents include compounds with 2 phenolic groups such as diphenyldichlorosilane, diphenylchlorosilane, diphenylfluorosilane, diphenylmethylchlorosilane, diphenylethylchlorosilane, diphenyldimethoxysilane, diphenylmethoxysilane, diphenylethoxysilane, diphenylmethylmethoxysilane, diphenylmethylethoxysilane and diphenyldiethoxysilane. These phenyl surface modification agents also include compounds with 3 phenolic groups such as triphenylchlorosilane, triphenylflourosilane, and triphenylethoxysilane. Another important phenyl compound, 1,3-diphenyltetramethyldisilazane, is an exception to this basic formula. These lists are not exhaustive, but do convey the basic nature of the group. The useful fluorocarbon based surface modification agents include (3,3,3-trifluoropropyl)trimethoxysilane), (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1dimethylchlorsilane, and other fluorocarbon groups that have a reactive group, such as Cl or OCH3)), that will form covalent bonds with a hydroxyl group.

The paragraph above lists some of the typical useful properties for many conventional applications. However, there are other potential applications for nanoporous dielectrics and aerogels that may have different desirable properties. Examples of some other potentially desirable properties include hydrophilicity, increased electrical conductivity, increased dielectric breakdown voltage, increased or decreased reactivity with certain chemicals, and increased volatility. This list is not exhaustive. However, it shows that, depending upon the application, many different types of properties may be desirable. Thus, it is clear that many other materials that will form covalent bonds with hydroxyl groups are potential surface modifiers that may impart other potentially desirable properties.

This invention also comprises the use of gelation catalysts, such as ammonium hydroxide. This also includes the allowance of other gelation catalysts in place of the ammonium hydroxide and/or for the gelation catalyst to be added after deposition. Typically, these alternate catalysts modify the pH of the sol. It is preferable to use catalysts that raise the pH, although acid catalysts can be used. Typically, acid catalysis results in longer processing times and a denser dielectric than a base catalyzed process. Some examples of other preferred gelation catalysts include ammonia, the volatile amine species (low molecular weight amines) and volatile fluorine species. When the catalyst is added after deposition, it is preferable to add the catalyst as a vapor, mist, or other vaporish form.

This invention allows production of nanoporous dielectrics at room temperature and atmospheric pressure, without a separate surface modification step. Although not required to prevent substantial densification, this new method does not exclude the use of supercritical drying or surface modification steps prior to drying. To the extent that the freezing rates are fast enough to prevent large (e.g., 50 nm) crystals, it is also compatible with freeze drying. In general, this new method is compatible with most prior art aerogel techniques.

Other examples of modifications involve the reaction atmosphere and/or temperature. Also coating and gelation need not be performed in the same chamber or even in the same atmosphere. For instance, the substrate may have its temperature lowered to retard gelation or elevated to speed surface modification and/or gelation. Also, total pressure and/or temperature may be varied to further control evaporation rates and/or gel time. Elevated temperature processing is typically performed at no less than 40(degree) C; however, 50(degree)C is preferred, and 70(degree)C is more preferred. When working at elevated temperatures, care should be taken (e.g., the partial pressures in the reaction atmosphere should be high enough) to prevent solvent boiling.

Although TEOS has been used as a representative example of a reactant, other metal alkoxides may be used either alone or in combination with TEOS or each other to form a silica network. These metal alkoxides include tetramethoxysilane (TMOS), methyltriethoxysilane (MTEOS), 1,2-Bis (trimethoxysilyl)ethane (BTMSE), combinations thereof, and other silicon-based metal alkoxides known in the art. A sol may also be formed from alkoxides of other metals known in the art such as aluminum and titanium. Some other precursor sols known in the art include particulate metal oxides and organic precursors. Two representative particulate metal oxides are pyrogenic (fumed) silica and colloidal silica. Some representative organic precursors are melamine, phenol furfural, and resorcinol. In addition to alternate reactants, alternate solvents may also be used. Some examples of preferred alternates for ethanol are methanol and the other higher alcohols. Other acids may be used as a precursor sol stabilizer in place of the nitric acid.

An additional modification is to allow and/or promote the formation of moderate sized (15 to 150 monomers per molecule) oligomers in the precursor sol. These larger oligomers may speed the gelation process in the deposited sol. A sol containing large oligomers may have a higher viscosity than a sol with small oligomers. However, as long as the viscosity is stable, this higher viscosity can be compensated by methods known in the art, such as adjusting solvent ratios and spin conditions. To help achieve this desired stable viscosity, the oligomerization may need to be slowed or substantially halted before deposition. Potential methods of promoting oligomerization might include heating the precursor sol, evaporating solvent, or adding small amounts of a gelation catalyst such as ammonium hydroxide. Potential methods of retarding oligomerization might include cooling the precursor sol, diluting the sol with asolvent, or restoring the precursor sol to a pH that minimizes condensation and gelation (Nitric acid could be used in conjunction with the ammonium hydroxide exemplified above).

Although the present invention has been described with several sample embodiments, various changes and modifications may be suggested to one skilled in the art. It is intended that the present invention encompass such changes and modifications as fall within the scope of the appended claims.

Specification:

This invention pertains generally to precursors for nanoporous (fine-pored) aerogel fabrication, and more particularly to precursors suitable for subcritical and supercritical drying of bulk and thin film aerogels.

BACKGROUND OF THE INVENTION

Aerogels are porous silica materials which can be used for a variety of purposes including as films (e.g. as electrical insulators on semiconductor devices or as optical coatings) or in bulk (e.g. as thermal insulators). For ease of discussion, the examples herein will be mainly of usage as electrical insulators on semiconductor devices.

Semiconductors are widely used in integrated circuits for electronic devices such as computers and televisions. Semiconductor and electronics manufacturers, as well as end users, desire integrated circuits which can accomplish more in less time in a smaller package while consuming less power. However, many of these desires are in opposition to each other. For instance, simply shrinking the feature size on a given circuit from 0.5 microns to 0.25 microns can increase energy use and heat generation by 30%. Miniaturization also generally results in increased capacitive coupling, or crosstalk, between conductors which carry signals across the chip. This effect both limits achievable speed and degrades the noise margin used to insure proper device operation. One way to reduce energy use/heat generation and crosstalk effects is to decrease the dielectric constant of the insulator, or dielectric, which separates conductors. US Patent 5,470,802, issued to Gnade et al., provides background on several of these

schemes.

A class of materials, nanoporous dielectrics, includes some of the most promising new materials for semiconductor fabrication. These dielectric materials contain a solid structure, for example of silica, which is permeated with an interconnected network of pores having diameters typically on the order of a few nanometers. These materials may be formed with extremely high porosities, with corresponding dielectric constants typically less than half the dielectric constant of dense silica. And yet despite their high porosity, it has been found that nanoporous dielectrics may be fabricated which have high strength and excellent compatibility with most existing semiconductor fabrication processes. Thus nanoporous dielectrics offer a viable low-dielectric constant replacement for common semiconductor dielectrics such as dense silica.

The preferred method for forming nanoporous dielectrics is through the use of sol-gel techniques. The word sol-gel does not describe a product but a reaction mechanism whereby a sol, which is a colloidal suspension of solid particles in a liquid, transforms into a gel due to growth and interconnection of the solid particles. One theory is that through continued reactions within the sol, one or more molecules in the sol may eventually reach macroscopic dimensions so that it/they form a solid network which extends substantially throughout the sol. At this point (called the gel point), the substance is said to be a gel. By this definition, a gel is a substance that contains a continuous solid skeleton enclosing a continuous liquid phase. As the skeleton is porous, the term "gel" as used herein means an open-pored solid structure enclosing a pore fluid.

One method of forming a sol is through hydrolysis and condensation reactions, which can cause a multifunctional monomer in a solution to polymerize into relatively large, highly branched particles. Many monomers suitable for such polymerization are metal alkoxides. For example, a tetraethoxysilane (TEOS) monomer may be partially hydrolyzed in water by the reaction Reaction conditions may be controlled such that, on the average, each monomer undergoes a desired number of hydrolysis reactions to partially or fully hydrolyze the monomer. TEOS which has been fully hydrolyzed becomes Si(OH) 4)). Once a molecule has been at least partially hydrolyzed, two molecules can then link together in a condensation reaction, such as or to form an oligomer and liberate a molecule of water or ethanol. The Si-O-Si configuration in the oligomer formed by these reactions has three sites available at each end for further hydrolysis and condensation. Thus, additional monomers or oligomers can be added to this molecule in a somewhat random fashion to create a highly branched polymeric molecule from literally thousands of monomers. An oligomerized metal alkoxide, as defined herein, comprises molecules formed from at least two alkoxide monomers, but does not comprise a gel.

Sol-gel reactions form the basis for xerogel and aerogel film deposition. In a typical thin film xerogel process, an ungelled precursor sol may be applied (e.g., spray coated, dip-coated, or spin-coated) to a substrate to form a thin film on the order of several microns or less in thickness, gelled, and dried to form a dense film. The precursor sol often comprises a stock solution and a solvent, and possibly also a gelation catalyst that modifies the pH of the precursor sol in order to speed gelation. During and after coating, the volatile components in the sol thin film are usually allowed to rapidly evaporate. Thus, the deposition, gelation, and drying phases may take place simultaneously (at least to some degree) as the film collapses rapidly to a dense film. In contrast, an aerogel process differs from a xerogel process largely by avoiding pore collapse during drying of the wet gel. Some methods for avoiding pore collapse include wet gel treatment with condensation-inhibiting modifying agents (as described in Gnade '802) and supercritical pore fluid extraction.

SUMMARY OF THE INVENTION

The present invention is directed to a metal-based aerogel precursor sol, comprising a metal-based

aerogel precursor sol, comprising an aerogel precursor reactant selected from the group consisting of metal alkoxides, at least partially hydrolyzed metal alkoxides, particulate metal oxides, and combinations thereof, and a polyol as a first solvent, the polyol being selected from the group of glycerol, ethylene glycol, 1,4-butylene glycol, 1,5-pentanediol, 1,2,4-butanetriol, 1,2,3-butanetriol, 2-methyl-propanetriol, 2-(hydroxymethyl)-1,3-propanediol, 1-4,1-4-butanediol, 2-methyl-1,3-propanediol, and combinations thereof, wherein, the molar ratio of said first solvent molecules to the metal atoms in said reactant is at least 1:16.

The invention further pertains to a non-supercritical method of forming a nonoporous aerogel, said method comprising the steps:

providing an aerogel precursor sol as defined in any one of claims 1 to 25, said sol being dispersed in said first solvent and a second solvent,

evaporating substantially all of said second solvent while preventing substantial evaporation of said first solvent, and allowing the sol to create a gel, wherein the gel comprises a porous solid and a pore fluid;

continuing to prevent substantial evaporation of said first solvent from said sol until a drying step,

wherein said drying step comprises forming a dry aerogel by removing the pore fluid in a non-supercritical drying atmosphere without substantial collapse of the porous solid;

whereby the skeletal density of the dry aerogel is determined approximately by the volume ratio of said aerogel precursor reactant to said first solvent in said aerogel precursor sol.

Between aerogels and xerogels, aerogels are the preferable of the two dried gel materials for semiconductor thin film nanoporous dielectric applications. Typical thin film xerogel methods produce films having limited porosity (up to 60% with large pore sizes, but generally substantially less than 50% with pore sizes useful in submicron semiconductor fabrication). While some prior art xerogels have porosities greater than 50%; these prior art xerogels had substantially larger pore sizes (typically above 100 nm). These large pore size gels have significantly less mechanical strength. Additionally, their large size makes them unsuitable for filling small (typically less than 1 (mu)m, and potentially less than 100 nm) patterned gaps on a microcircuit and limits their optical film uses to only the longer wavelengths. A nanoporous aerogel thin film, on the other hand, may be formed with almost any desired porosity coupled with a very fine pore size. Generally, as used herein, nanoporous materials have average pore sizes less than about 25 nm across, but preferably less than 20 nm (and more preferably less than 10 nanometers and still more preferably less than 5 nanometers). In many formulations using this method, the typical nanoporous materials for semiconductor applications may have average pore sizes at least 1 nm across, but more often at least 3 nm. The nanoporous inorganic dielectrics include the nanoporous metal oxides, particularly nanoporous silica.

In many nanoporous thin film applications, such as aerogels and xerogels used as optical films or in microelectronics, the precise control of film thickness and aerogel density are desirable. Several important properties of the film are related to the aerogel density, including mechanical strength, pore size and dielectric constant. It has now been found that both aerogel density and film thickness are related to the viscosity of the sol at the time it is applied to a substrate. This presents a problem which was heretofore unrecognized. This problem is that with conventional precursor sols and deposition methods, it is extremely difficult to control both aerogel density and film thickness independently and accurately.

Nanoporous dielectric thin films may be deposited on patterned wafers, often over a level of patterned conductors. It has now been recognized that sol deposition should be completed prior to the onset of gelation to insure that gaps between such conductors remain adequately filled and that the surface of the gel remains substantially planar. To this end, it is also desirable that no significant evaporation of pore fluid occur after gelation, such as during aging. Unfortunately, it is also desirable that the gel point be reachable as soon after deposition as possible to simplify processing, and one method for speeding gelation of thin films is to allow evaporation to occur. It is recognized herein that a suitable precursor sol for aerogel deposition should allow control of film thickness, aerogel density, gap fill and planarity, and be relatively stable prior to deposition, and yet gel relatively soon after deposition and age without substantial evaporation.

A method has now been found which allows controlled deposition of aerogel thin films from a multi-solvent precursor sol. In this method, sol viscosity and film thickness may be controlled relatively independently. This allows film thickness to be rapidly changed from a first known value to a second known value which can be set by solvent ratios and spin conditions, thus keeping film thickness largely independent of aerogel density and allowing rapid gelation. However, at the same time, the solid:liquid ratio present in the film at drying (and therefore the aerogel density) can be accurately determined in the precursor sol prior to deposition, independent of spin conditions and film thickness.

Even with this novel separation of the deposition problem into viscosity control and density control subproblems, our experience has been that thin film sol-gel techniques for forming xerogels and aerogels generally require some method, such as atmospheric control, to limit evaporation before drying, such as after gelation and during aging. In principle, this evaporation rate control can be accomplished by controlling the solvent vapor concentration above the wafer. However, our experience has shown that the solvent evaporation rate is very sensitive to small changes in the vapor concentration and temperature. In an effort to better understand this process, we have modeled the isothermal vaporization of several solvents from a wafer as a function of percent saturation. The ambient temperature evaporation rates for some of these solvents are given in Figure 1. For evaporation to not be a processing problem, the product of the evaporation rate and processing time (preferably on the order of minutes) should be significantly less than the film thickness. This suggests that for solvents such as ethanol, the atmosphere above the wafer would have to be maintained at over 99% saturation. However, there can be problems associated with allowing the atmosphere to reach saturation or supersaturation. Some of these problems are related to condensation of an atmospheric constituent upon the thin film. Condensation on either the gelled or ungelled thin film has been found to cause defects in an insufficiently aged film. Thus, it is generally desirable to control the atmosphere such that no constituent is saturated.

Rather than using a high volatility solvent and precisely controlling the solvent atmosphere, we have discovered that a better solution is to use a low volatility solvent with less atmospheric control. Upon investigating this premise, we have discovered that glycerol makes an excellent solvent.

The use of glycerol allows a loosening (as compared to prior art solvents) of the required atmospheric control during deposition, gelation, and/or aging. This is because, that even though saturation should still preferably be avoided, the atmospheric solvent concentration can be lowered without excessive evaporation. Figure 2 shows how the evaporation rate of glycerol varies with temperature and atmospheric solvent concentration. It has been our experience that, with glycerol, acceptable gels can be formed by depositing, gelling and aging in an uncontrolled or a substantially uncontrolled atmosphere.

In the production of nanoporous dielectrics it is preferable to subject the wet gel thin film to a process known as aging. Hydrolysis and condensation reactions do not stop at the gel point, but continue to restructure, or age, the gel until the reactions are purposely halted. It is believed that during aging, preferential dissolution and redeposition of portions of the solid structure produce beneficial results,

including higher strength, greater uniformity of pore size, and a greater ability to resist pore collapse during drying. Unfortunately, we have now found that conventional aging techniques used for bulk gels are poorly suited for aging thin films in semiconductor processing, partly because they generally require liquid immersion of the substrate and partly because they require days or even weeks to complete. One aspect of this invention includes a vapor phase aging technique that avoids liquid immersion or premature drying of the wet gel thin film and that, surprisingly, can age such a thin film in a matter of minutes.

Again, aerogels are nanoporous materials which can be used for a variety of purposes including as films or in bulk. It should be noted, however, the problems incurred in film fabrication processing is so different from bulk processing problems, that, for practical purposes, film processing is not analogous to bulk processing.

Generally, we have now found that aging in a saturated atmosphere avoids the difficulties encountered with liquid immersion aging. Furthermore, this aspect of the invention provides several approaches for aging wet gels at increased temperatures. These methods may be used even when the wet gel originally contains low boiling point pore liquids. However, they work better with low volatility solvents. Finally, this aspect of the invention provides for adding an optional vapor phase aging catalyst to the aging atmosphere to speed aging.

Aging a wet gel in thin film form is difficult, as the film contains an extremely small amount of pore fluid that should be held fairly constant for a period of time in order for aging to occur. If pore fluid evaporates from the film before aging has strengthened the network, the film will tend to densify in xerogel fashion. On the other hand, if excess pore fluid condenses from the atmosphere onto the thin film before the network has been strengthened, this may locally disrupt the aging process and cause film defects.

Thus, we now know that some method of pore fluid evaporation rate control during aging is beneficial to aerogel thin film fabrication. In principle, evaporation rate control during aging can be accomplished by actively controlling the pore fluid vapor concentration above the wafer. However, the total amount of pore fluid contained in, for instance, a 1 mm thick 70% porous wet gel deposited on a 150 mm wafer is only about 0.012 mL, an amount that would easily fit in a single 3 mm diameter drop of fluid. Typical thin films used for nanoporous dielectrics on semiconductor wafers are approximately 1000 times thinner. Thus, actively controlling the pore fluid vapor concentration (by adding or removing solvent to the atmosphere) to allow no more than, e.g., 1%, or less, pore fluid evaporation during aging presents a difficult proposition; the surface area of the thin film is high and the allowable tolerance for pore fluid variations is extremely small. In particular, evaporation and condensation control are especially important for rapid aging at elevated temperature, where film production processes have heretofore apparently not been practically possible.

We have overcome the evaporation rate control problem by not attempting to actively control pore fluid vapor concentration above a wafer at all. Instead, the wafer is processed in an extremely low-volume chamber, such that through natural evaporation of a relatively small amount of the pore fluid contained in the wet gel film, the processing atmosphere becomes substantially saturated in pore fluid. Unless the wafer is cooled at some point in a substantially saturated processing atmosphere, this method also naturally avoids problems with condensation, which should generally be avoided, particularly during high temperature processing.

A metal-based nanoporous aerogel precursor sol is disclosed herein. This nanoporous aerogel precursor sol comprises a metal-based aerogel precursor reactant and a first solvent comprising a first polyol; wherein, the molar ratio of the first solvent molecules to the metal atoms in the reactant is at least 1 : 16 .

Preferably, the first polyol is glycerol. Preferably, the aerogel precursor reactant may be selected from the group consisting of metal alkoxides, at least partially hydrolyzed metal alkoxides, particulate metal oxides, and combinations thereof. Typically, the molar ratio of the first solvent molecules to the metal atoms in the reactant is no greater than 12 : 1, and preferably, the molar ratio of the first solvent molecules to the metal atoms in the reactant is between 1 : 2 and 12 : 1. In some embodiments, the molar ratio of the first solvent molecules to the metal atoms in the reactant is between 2.5 :1 and 12:1. In this method, it is also preferable that the nanoporous dielectric has a porosity greater than 60% and an average pore diameter less than 25 nm. In some embodiments, the aerogel precursor also comprises a second solvent. Preferably, the second solvent has a boiling point lower than glycerol's. In some embodiments, the second solvent may be ethanol. In some embodiments, the first solvent also comprises a glycol, preferably selected from the group consisting of ethylene glycol, 1,4 butylene glycol, 1,5 pentanediol, and combinations thereof. In some embodiments, the first polyol is selected from the group consisting of 1,2,4-butanetriol; 1,2,3- butanetriol; 2 methyl-propanetriol; and 2-(hydroxymethyl)-1,3-propanediol; 1-4, 1-4, butanediol; and 2-methyl-1,3-propanediol, and combinations thereof. In some embodiments, the first polyol is a glycol selected from the group consisting of ethylene glycol, 1,4 butylene glycol, 1,5 pentanediol, and combinations thereof.

Thus, this invention allows controlled porosity thin film nanoporous aerogels to be deposited, gelled, aged, and dried without atmospheric controls. In another aspect, this invention allows controlled porosity thin film nanoporous aerogels to be deposited, gelled, rapidly aged at an elevated temperature, and dried with only passive atmospheric controls, such as limiting the volume of the aging chamber.

A method for forming a thin film nanoporous dielectric on a semiconductor substrate is disclosed herein. This method comprises the steps of providing a semiconductor substrate and depositing an nanoporous aerogel precursor sol upon the substrate. This aerogel precursor sol comprises a metal-based aerogel precursor reactant and a first solvent comprising glycerol; wherein, the molar ratio of the molecules of glycerol to the metal atoms in the reactant is at least 1 : 16 . The method further comprises allowing the deposited sol to create a gel, wherein the gel comprises a porous solid and a pore fluid; and forming a dry, nanoporous dielectric by removing the pore fluid in a drying atmosphere without substantially collapsing the porous solid. In this method, the pressure of the drying atmosphere during the forming step is less than the critical pressure of the pore fluid, preferably near atmospheric pressure.

Preferably, the aerogel precursor reactant may be selected from the group consisting of metal alkoxides, at least partially hydrolyzed metal alkoxides, particulate metal oxides, and combinations thereof. Preferably, the aerogel precursor reactant comprises silicon. In some embodiments, the aerogel precursor reactant is TEOS. Typically, the molar ratio of the molecules of glycerol to the metal atoms in the reactant is no greater than 12 : 1, and preferably, the molar ratio of the molecules of glycerol to the metal atoms in the reactant is between 1 : 2 and 12 : 1. In some embodiments, the molar ratio of the molecules of glycerol to the metal atoms in the reactant is between 2.5 :1 and 12:1. In this method, it is also preferable that the nanoporous dielectric has a porosity greater than 60% and an average pore diameter less than 25 nm. In some embodiments, the aerogel precursor also comprises a second solvent. Preferably, the second solvent has a boiling point lower than glycerol's. In some embodiments, the second solvent may be ethanol. In some embodiments, the first solvent also comprises a glycol, preferably selected from the group consisting of ethylene glycol, 1,4-butylene glycol, 1,5-pentanediol, and combinations thereof. After aging but before drying, in some embodiments, the aging fluid is replaced by a drying fluid. This allows, e.g., rapid, lower temperature (e.g., room temperature) drying with a fluid that evaporates faster and has a suitably low surface tension. Examples of drying fluids include heptane, ethanol, acetone, 2-ethylbutyl alcohol and some alcohol-water mixtures.

Thus, this invention allows controlled porosity thin film nanoporous aerogels to be deposited, gelled, aged, and dried without atmospheric controls. In another aspect, this invention allows controlled

porosity thin film nanoporous aerogels to be deposited, gelled, rapidly aged at an elevated temperature, and dried with only passive atmospheric controls, such as limiting the volume of the aging chamber.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention, including various features and advantages thereof, may be best understood with reference to the following drawings, wherein:

Figure 1 contains a graph of the variation of evaporation rate with saturation ratio and solvent type.

Figure 2 contains a graph of the evaporation rate for glycerol a function of temperature and atmospheric saturation ratio.

Figure 3 contains a graph of the theoretical relationship between porosity, refractive index, and dielectric constant for nanoporous silica dielectrics.

Figure 4 contains a graph of the change in gel times (without solvent evaporation) for bulk ethylene glycol-based gels as a function of base catalyst

Figure 5 contains a graph of the variation of modulus with density for a non-glycol-based gel and an ethylene glycol-based gel.

Figure 6 contains a graph showing the distribution of pore sizes of a bulk glycerol-based nanoporous dielectric according to the present invention.

Figure 7 contains a graph of the evaporation rate for ethylene glycol as a function of temperature and atmospheric saturation ratio.

Figure 8 contains a graph showing the change in vapor pressure with temperature.

Figure 9 contains a graph showing the shrinkage of a thin film when dried in a 5 mm thick container.

Figure 10 contains a graph showing the shrinkage of a thin film when dried in a 1 mm thick container.

Figures 11A-11B contain graphs of the viscosity variation as a function of alcohol volume fraction for some ethylene glycol/alcohol and glycerol/alcohol mixtures.

Figures 12A-12B contain cross-sections of a semiconductor substrate at several points during deposition of a thin film according to the present invention.

Figure 13 is a flow chart of a deposition process for a nanoporous dielectric according to the present invention.

Figure 14 contains a graph of the theoretical molar ratio of glycerol molecules to metal atoms vs. porosity of a nanoporous dielectric according to the present invention.

Figure 15 contains a graph of relative film thickness and relative film viscosity as a function of time for one embodiment of the present invention.

Figures 16A and 16B contain, respectively, a cross-sectional and a plan view of a sol-gel thin film

processing apparatus according to the present invention.

Figure 16C contains a cross-sectional view of the same apparatus in contact with a substrate.

Figures 17A and 17B contain, respectively, cross-sectional views of another apparatus according to the present invention, empty and enclosing a substrate.

Figures 18A and 18B contain, respectively, cross-sectional views of yet another apparatus according to the present invention, empty and enclosing a substrate.

Figures 19A, 19B and 19C contain cross-sectional views of additional apparatus configurations which illustrate other aspects of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Typical sol-gel thin film processes produce gels which collapse and densify upon drying, thus forming xerogels having only a few percent porosity. Under the uncontrolled drying conditions of xerogel film formation, it has been neither critical nor possible to completely separate the deposition, aggregation, gelation, and drying steps during formation of the thin film, as the entire process may be completed in a few seconds. However, it has now been found that such methods are generally unsuited for depositing high porosity thin films with a controllable low density; because in an aerogel type drying process, the film remains substantially undensified after drying, its final density is largely determined by the solid:liquid ratio in the film at the gel time. It has now been discovered that the following criteria are desirable for aerogel thin film deposition, particularly where the thin film is required to planarize and/or gap fill a patterned wafer:

1) an initial viscosity suitable for spin-on application

2) stable viscosity at deposition

3) stable film thickness at gel time

4) a predetermined solid:liquid ratio at gel time

5) gelation shortly after deposition No prior art precursor sol and method have been found which meet these conditions. However, in accordance with the present invention, it has now been found that a sol prepared with at least two solvents in specific ratios may be used to meet these conditions.

The method of depositing and gelling such a precursor sol can be best understood with reference to Figure 15.

As shown in Figure 15 for time t=0, a multi-solvent precursor sol may be spun onto a wafer at an initial film thickness D0 and an initial viscosity h0. This is preferably done in a controlled atmosphere having a partial pressure of the low volatility solvent which greatly retards evaporation of the low volatility solvent from the wafer. Thus after spin-on application, the high volatility solvent is preferentially removed from the wafer during evaporation time period T1 while the low volatility solvent is maintained, thereby decreasing the film thickness to D1. Viscosity also changes during this time to h1, preferably due primarily to the removal of solvent. Ideally, little cross-linking of polymeric clusters in the sol occurs during this time. At the end of T1, substantially all of the high volatility solvent should be evaporated, at which time film thickness should stabilize or proceed to shrink at a much reduced rate,

thereby providing a predetermined liquid:solid ratio and thickness for the thin film at gel time.

Time period T2 has the primary purpose of providing separation between the endpoint of evaporation time period T1 and the gel point which occurs during gelation time period T3. Preferably, time period T2 is greater than 0. However, some precursors, particularly those with solvents such as glycerol, that promote faster gelation, will gel toward the end of period T1. Additionally, during time period T1 or T2 a vapor-phase catalyst such as ammonia may be introduced into the controlled atmosphere. This catalyst may diffuse into the thin film, further activating the sol and promoting rapid cross-linking. Although little or no evaporation preferably takes place during T2, viscosity should begin to increase substantially as cross-linking continues to link polymeric clusters.

Evaporation after the gel point may result in poor gap-fill and planarity for patterned wafers. Consequently, after gelation time period T3, film thickness is preferably held nearly constant until the gel point has passed by limiting evaporation. Sometime during time period T3, a marked change in viscosity occurs as the sol nears the gel point, where large polymeric clusters finally join to create a spanning cluster which is continuous across the thin film.

Several advantages of this new approach are apparent from Figure 15. Sol viscosity and film thickness are both allowed to change rapidly, but generally not at the same time. Also, film thickness is changed from a first known value to a second known value which can be independently set by solvent ratios and spin conditions. Using this method, a low viscosity film may be applied, quickly reduced to a preset thickness, and rapidly gelled at a desired density.

The preceding paragraphs teach a method of varying the precursor sol viscosity independently of the dried gel density. However, it still leaves open the question of which solvents are most appropriate. Our experience shows that the solvent evaporation rate for traditional aerogel solvents is very sensitive to small changes in the vapor concentration and temperature. In an effort to better understand this process, we have modeled isothermal solvent vaporization from a wafer as a function of percent saturation. This modeling is based on mass transfer theory. Transport Phenomena, (particularly Chapters 16 and 17) by R. B. Bird, W. E. Stewart, and E. N. Lightfoot, is a good reference for mass transfer theory. These calculations were performed for a range of solvents. The ambient temperature evaporation rates for some of these solvents are given in Figure 1. For evaporation to not be a processing problem, the product of the evaporation rate and processing time (preferably on the order of minutes) should be significantly less than the film thickness. This suggests that for solvents such as ethanol, the atmosphere above the wafer would have to be maintained at over about 99% saturation. However, there can be problems associated with allowing the atmosphere to reach saturation or supersaturation. Some of these problems are related to condensation of an atmospheric constituent upon the thin film. Condensation on either the gelled or ungelled thin film has been found to cause defects in an insufficiently aged film. Thus, it is generally desirable to control the atmosphere such that no constituent is saturated.

Rather than using a high volatility solvent and precisely controlling the solvent atmosphere, we have discovered that a better solution is to use a low volatility solvent with less atmospheric control. Upon investigating this premise, we have discovered that glycerol makes an excellent solvent.

The use of glycerol allows a loosening (as compared to prior art solvents) of the required atmospheric control during deposition and/or gelation. This is because, that even though saturation should still preferably be avoided, the atmospheric solvent concentration can be lowered without excessive evaporation. Figure 2 shows how the evaporation rate of glycerol varies with temperature and atmospheric solvent concentration. It has been our experience that, with glycerol, acceptable gels can be formed by depositing and gelling in an uncontrolled or a substantially uncontrolled atmosphere. In this most preferred approach, (a substantially uncontrolled atmosphere) atmospheric controls, if any, during

deposition and gelation are typically limited to cleanroom temperature and humidity controls, although the wafer and/or precursor sol may have independent temperature controls.

One attractive feature of using glycerol as a solvent is that at ambient temperature, the evaporation rate is sufficiently low so that several hours at ambient conditions will not yield dramatic shrinkage for thin films. It has been our experience that with glycerol, acceptable gels can be formed by depositing, gelling, and aging in an uncontrolled or a substantially uncontrolled atmosphere. With glycerol, the ambient temperature evaporation rate is sufficiently low so that several hours at ambient conditions will not yield dramatic shrinkage for thin films. It has also been our experience that with ethylene glycol, acceptable gels can be formed by depositing, and gelling an uncontrolled or a substantially uncontrolled atmosphere. With ethylene glycol, the ambient temperature evaporation rate is higher than glycerol, but still sufficiently low so that several minutes at ambient conditions will not yield dramatic shrinkage for thin films. However, the ethylene glycol-based sols have significantly lower viscosities than comparable glycerol-based sols, thus simplifying deposition. Also, the pore fluids in glycerol-based sols have significantly higher surface tensions than comparable ethylene glycol-based sols, thus making low shrinkage drying more difficult.

In addition to serving as a low vapor pressure and water-miscible solvent, ethylene glycol and glycerol may also participate in sol-gel reactions. Although the exact reactions in this process have not been fully studied, some reactions can be predicted. If tetraethoxysilane (TEOS) is employed as a precursor, ethylene glycol can exchange with the ethoxy groups:

Similarly, if tetraethoxysilane (TEOS) is employed as a precursor with a glycerol solvent, the glycerol can exchange with the ethoxy groups:

In principle, the presence and concentration of these chemical groups can change the precursor reactivity (i.e., gel time), modify the gel microstructure (surface area, pore size distribution, etc.), change the aging characteristics, or change nearly any other characteristic of the gel.

The use of a new solvent system can change a wide range of processing parameters including gel time, viscosity, aging conditions and drying shrinkage. Many of these properties such as gel times are difficult to measure on thin films. Although bulk and thin film properties may be different, it is often useful to perform a series of experiments on bulk samples (e.g. approximately 5 mm diameter by 30 mm long) to provide a better understanding of how changing solvent systems affects the nanoporous silica process.

Glycerol can react with TEOS and produce a dried gel with surprisingly different properties than that of an ethanol/TEOS gel. Unanticipated property changes in the glycerol/TEOS based gels generally include (at least on most formulations):

Lower density is achievable without supercritical drying or pre-drying surface modification

Greatly simplified aging

Shorter gel times even without a catalyst

Strengths of bulk samples which are approximately an order of magnitude greater (at a given density) than conventional TEOS gels

Very high surface area ((equivalent to)1,000 m2)/g)

High optical clarity of bulk samples (This is likely due to a narrow pore size distribution)

Low density -- With this invention, it is possible to form dried gels at very low densities without pre-drying surface modification or supercritical drying. These low densities can generally be down around .3 to .2 g/cm3) (non-porous SiO2)) has a density of 2.2g/cm3)), or with care, below .1 g/cm3). Stated in terms of porosity (porosity is the percentage of a structure which is hollow), this denotes porosities of about 86% and 91% (about 95% porosity with a density of .1 g/cm3)). As shown in Figure 3, these porosities correspond to dielectric constants of about 1.4 for the 86% porous, and 1.2 for 91% porous. The actual mechanism that allows these high porosities is not fully known. However, it may be because the gels have high mechanical strength, because the gels do not have as many surface OH (hydroxyl) groups, a combination of these, or some other factors. This method also seems to obtain excellent uniformity across the wafer.

If desired, this process can be adjusted (by varying the TEOS/solvent ratios) to give any porosity from above 90% down to about 50%. Typical prior art dried gels with small pore sizes required either supercritical drying or a surface modification step before drying to achieve these low densities. While some prior art xerogels have porosities greater than 50%; these prior art xerogels had substantially larger pore sizes (typically above 100 nm). These large pore size gels have significantly less mechanical strength. Additionally, their large size makes them unsuitable for filling small (typically less than 1 (mu) m) patterned gaps on a microcircuit. If desired, this process can also be adjusted (by varying the TEOS/solvent ratios) to provide porosities below 50%. Porosities down to 20% are possible when care is taken to prevent premature gelation.

Thus, this invention has enabled a new, simple nanoporous low density dielectric fabrication method. This new glycerol-based method allows both bulk and thin film aerogels to be made without supercritical drying, or a surface modification step before drying. Prior art aerogels have required at least one of these steps to prevent substantial pore collapse during drying. Density Prediction - By varying the ratio of glycerol to silicon (or other metal), the density after drying can be accurately predicted. This accuracy is likely due to the well controlled evaporation allowed by the low volatility glycerol solvent. As our process shows excellent shrinkage control during aging and drying, this allows accurate prediction of the density (and thus porosity) of the dried gel. Although density prediction had not generally been considered a large problem with bulk gels, it had typically been difficult to predict the final porosity of thin film gels. This accurate density prediction, even for low porosity dried gels, is one reason why this new process might be preferred over existing xerogel processes for forming low porosity gels.

Simplified Aging -- We have found that in the production of nanoporous dielectrics it is preferable to subject the wet gel thin film to a process known as aging. Hydrolysis and condensation reactions do not stop at the gel point, but continue to restructure, or age, the gel until the reactions are purposely halted. It is believed that during aging, preferential dissolution and redeposition of portions of the solid structure produce beneficial results. These beneficial results include higher strength, greater uniformity of pore size, and a greater ability to resist pore collapse during drying. However, aging a wet gel in thin film form is difficult, as the film contains an extremely small amount of pore fluid that should be held fairly constant for a period of time in order for aging to occur. If pore fluid evaporates from the film before aging has strengthened the network, the film will tend to densify in xerogel fashion. On the other hand, if excess pore fluid condenses from the atmosphere onto the thin film before the network has been strengthened, this may locally disrupt the aging process and cause film defects.

Our new, glycerol-based process has radically simplified aging of thin film nanoporous dielectrics. Other thin film nanoporous dielectric aging processes have either allowed significant evaporation, fluid condensation, or required a controlled aging atmosphere. During deposition and gelation, at least to

some degree, these glycerol-based processes behave similarly to the ethylene glycol-based processes described below. However, the ethylene glycol-based gels typically require atmospheric controls to prevent significant evaporation during aging, even at room temperature. In contrast, the glycerol-based gels have dramatically lower evaporation and shrinkage rates during aging. This allows atmospheric control to be loosened or eliminated during aging. We can fabricate high quality, thin film, glycerol-based nanoporous dielectrics with only passive atmospheric controls during room temperature or high temperature aging.

Shorter Gel Times -- The use of glycerol also substantially shortens the gel time. Many typical ethanol-based precursors have gel times of at least 400 seconds, when catalyzed (much longer w/o catalysis). However, we discovered that some glycerol-based precursors will gel during wafer spin-on, even without catalysis. This quick gelation is not only faster than an ethanol-based gel, but also surprisingly faster than an ethylene glycol-based gel. Figure 4 shows gel times for two different ethylene glycol-based compositions as a function of the amount of ammonia catalyst used. These gel times are for bulk gels for which there is no evaporation of ethanol and/or water as there would be for thin films. Evaporation increases the silica content and thus, decreases the gel time. Therefore, these gel times may be the upper limit for a given precursor/catalyst. The gel times reported in Figure 4 are approximately an order of magnitude shorter than conventional ethanol-based precursors. Gel times generally also exhibit a first order dependence on the concentration of ammonia catalyst. This implies that it may be possible to easily control the gel times.

For thin films of these new glycerol-based gels, it is routine to obtain gelation within seconds, even without a gelation catalyst. We have identified several mechanisms that can be used to launch gelation in thin films, without the addition of a catalyst. One method is the concentration of the precursor sol by allowing a volatile solvent to evaporate. Another method is increasing the pH by allowing an acid in the precursor sol to evaporate. This evaporative basification relies on increasing the precursor sol pH to help initiate gelation. However, this basification process does not typically require a pH change from below 7 to above 7. This evaporative basification acts similarly to a typical base catalysis process, greatly speeding gelation. At room temperature and pressure, some acids, such as nitric acid, have evaporation rates comparable to ethanol. Varying the concentrations and/or types of the high volatility solvent(s) and/or stabilizing acid provides a simple, yet tremendous flexible method for adjusting the gelation time.

Higher Strength -- The properties of the glycerol-based samples appear to be quite different from regular gels as evidenced by both their low degree of drying shrinkage and differences in qualitative handling of the wet and dry gels. Thus, upon physical inspection, the glycerol-based dried gels seem to have improved mechanical properties as compared to both conventional and ethylene glycol-based dried gels. Figure 5 shows the bulk modulus measured during isostatic compaction measurements of one sample prepared using one ethylene glycol-based and one conventional ethanol-based dried bulk gel (both have the same initial density). After initial changes attributed to buckling of the structure, both samples exhibit power law dependence of modulus with density. This power law dependence is usually observed in dried gels. However, what is surprising is the strength of the ethylene glycol-based dried gel. At a given density (and thus, dielectric constant), the modulus of this sample of the ethylene glycol dried gel is an order of magnitude higher than the conventional dried gel. Preliminary evaluations show that the glycerol-based gels are even stronger than the ethylene glycol-based gels. These evaluations include qualitative handling tests and information based on the shrinkage during drying. The reasons for this strength increase are not totally clear. However, preliminary experiments indicate that our rapid gelation times and/or narrow pore size distribution may be responsible for the high strengths.

High surface area -- We measured the surface areas of some dried bulk gels. These surface areas were on the order of 1,000 m2)/g, as compared to our typical ethanol-based dried gels which have surface areas in the 600-800 m2)/g range. These higher surface areas may imply smaller pore size and improved

mechanical properties. It is unclear at this time why these higher surface areas are obtained with the glycerol-based dried gels.

Pore size distribution -- The optical clarity of these dried bulk gels was greater than any ethanol-based dried gels at this density that we have previously made. It is possible that this excellent optical clarity is due to a very narrow pore size distribution. However, it is unclear why the glycerol has this effect. Preliminary experiments show that one possible explanation is that rapid gelation times may be linked to a narrow pore size distribution. Figure 6 shows the pore size distribution (as measured by BJH nitrogen desorption measurements) of a bulk gel sample with a density of about .57 g/cm3). The mean pore diameter (desorption method) of this sample was 3.76 nm. As the typical pores are not truly cylindrical, diameter, as used herein, actually refers to the diameter of an equivalent cylinder with the same surface area to volume ratio as the overall gel's surface area to volume ratio.

As shown above, some properties of the glycerol-based gels apply to both bulk gels and thin films. However, some advantages are most evident when applied to thin films, such as nanoporous dielectric films on semiconductor wafers. One important advantage is that this new method allows high quality nanoporous films to be processed with no atmospheric controls during deposition or gelation.

Although it is important to be able to deposit and gel thin nanoporous films without atmospheric controls, it is also desirable to age thin nanoporous films without atmospheric controls. It has been discovered that this can present a bigger challenge than deposition. The primary reason is that while deposition and room temperature gelation can take place in minutes, or even seconds; room temperature aging typically requires hours. Thus, an evaporation rate that provides acceptable shrinkage for a short process, may cause unacceptable shrinkage when the process times are lengthened by an order of magnitude.

As an example, we have found that with some glycerol-based gels, a satisfactory aging time at room temperature is on the order of a day. However, Table 1 shows that, by using higher temperatures, we can age thin films with times on the order of minutes. These aging times are comparable to the preferred aging time of many typical ethanol-based and ethylene glycol-based gels. Thus, when these times and temperatures are combined with the evaporation rates of Figure 1, Figure 7, and Figure 2, they give the approximate thickness loss during aging as shown in Table 2. These estimated thickness losses need to be compared with acceptable thickness losses, particularly for thin film applications. While no firm guidelines for acceptable thickness loss exist, one proposed guideline, for some microcircuit applications such as nanoporous dielectrics, is that the thickness losses should be less than 2% of the film thickness. For a hypothetical nominal film thickness of 1 (mu)m (Actual film thicknesses may typically vary from significantly less than .5 (mu)m to several (mu)m thick), this gives an allowable thickness loss of 20 nm. As shown in Table 2, the glycerol-based gels can achieve this preliminary goal without atmospheric control at room temperature. Thus, this invention allows controlled porosity thin film nanoporous aerogels to be deposited, gelled, aged, and dried without atmospheric controls. In another aspect, this invention allows controlled porosity thin film nanoporous aerogels to be deposited, gelled, rapidly aged at an elevated temperature, and dried with only passive atmospheric controls, such as limiting the volume of the aging chamber.

Improved yield and reliability considerations may require thickness losses below 2%, such as less than .5% or .1%. By using passive atmospheric control, this invention can be extended to these, and even lower evaporation losses. This passive control involves placing the gel in a relatively small closed container, at least during aging. In this aspect of the invention, evaporation from the wafer acts to raise the saturation ratio of the atmosphere inside the closed container. At any given temperature, this evaporation continues until the partial pressure of the vapor increases enough to equal the vapor pressure of the liquid. Thus, solvent/temperature combinations with lower vapor pressure will not allow as much

liquid solvent to evaporate as a higher vapor pressure combination allows. Figure 8 shows how vapor pressure varies with temperature for several solvents. If the container size is known, the amount of evaporation can be calculated. Figure 9 shows an estimate of how thick of layer of solvent could potentially be evaporated if a 70% porous gel is placed in a 5 mm high cylindrical container that is the same diameter as the wafer. Figure 10 shows a similar estimate for a container with a 1 mm high airspace above the wafer. These figures show that, with a 5 mm high airspace, the 20 nm preliminary goal is feasible up to 120 degrees C for glycerol-based gels, but only up to 50 degrees C for ethylene glycol-based gels. With the 1 mm airspace, the 20 nm goal is feasible all the way up to 150 degrees C for the glycerol-based gels, but only up to 80 degrees C for the ethylene glycol-based gels. Of course, lower temperature processing allows less evaporation. Passive evaporation control using the 1 mm containers allows less than 1 nm of thickness loss (.1% of a 1(mu)m thick film) for the glycerol-based gels, even at 100 degrees C.

There are many variations on this passive control approach. One variation allows the container size to increase. The thickness loss will linearly increase with the container volume. However, even a 1000 cubic centimeter container typically allows only 5 nm of glycerol evaporation at 80 degrees C. Another variation is the gel porosity. Higher porosity gels generally experience greater thickness losses while lower porosity gels generally experience slightly smaller thickness losses.

One disadvantage of glycerol is its relatively high viscosity which can cause problems with gap-filling and/or planarization. As described above, a low viscosity, high volatility solvent can be used to lower the viscosity. Figure 11A shows the calculated viscosity of some ethanol/glycerol and methanol/glycerol mixtures at room temperature. As the figure shows, alcohol can significantly reduce the viscosity of these mixtures. Figure 11B shows the calculated viscosity of some ethanol/ethylene glycol and methanol/ethylene glycol mixtures at room temperature. As this figure shows, the ethylene glycol is much less viscous than the glycerol, and small quantities of alcohol significantly reduce the viscosity of these mixtures. Also, if the viscosity using ethanol in the stock solution is higher than desired, further improvement can be realized by employing methanol in the precursor solution. The viscosities reported in Figures 11A-11B are for pure fluid mixtures only. In fact, depending upon the film precursor solution, the precursor solution might contain glycerol, alcohol, water, acid and partially reacted metal alkoxides. Of course, the viscosity can be increased before deposition by catalyzing the condensation reaction and hence, the values reported in Figures 11A-11B represent lower bounds.

This multi-solvent approach may be combined with or replaced by an alternative approach. This alternate approach use elevated temperatures to reduce the sol viscosity during application. By heating and/or diluting the precursor during deposition, (such as by heating the transfer line and deposition nozzle of a wafer spin station) the viscosity of the precursor sol can be substantially lowered. Not only does this preheat lower the sol viscosity, it will also speed gel times and accelerate the evaporation of any high volatility solvents. It may also be desirable to preheat the wafer. This wafer preheat should improve process control and may improve gap fill, particularly for the more viscous precursors. However, for many applications, wafer preheat is not required, thus simplifying process flows. When using a spin-on application method with this no wafer preheat approach, the spin station would not require a temperature controlled spinner.

Dried gels produced with this simple thin film aerogel fabrication process can be used in many applications. Some of these uses may not have been cost effective using prior art methods. These uses include low dielectric constant thin films (particularly on semiconductor substrates), miniaturized chemical sensors, thermal isolation structures, and thermal isolation layers (including thermal isolation structures for infrared detectors). As a general rule, many low dielectric constant thin films prefer porosities greater than 60%, with critical applications preferring porosities greater than 80 or 90%, thus giving a substantial reduction in dielectric constant. However, structural strength and integrity

considerations may limit the practical porosity to no more than 90%. Some applications, including thermal isolation structures and thermal isolation layers, may need to sacrifice some porosity for higher strength and stiffness. These higher stiffness requirements may require dielectrics with porosities as low as 30 or 45%. In other high strength/toughness applications, especially sensors, where surface area may be more important than density, it may be preferable to use a low porosity gel with a porosity between 20% and 40%.

The thin film discussion above has centered around thin film aerogels for microelectronic circuits. However, aerogels are also useful in other applications, such as thin films on passive substrates. These new high strength, easy to fabricate gels now make many of these uses practical. For purposes of this application, a passive substrate is defined as a substrate that does not comprise or contain a microelectronic circuit, or at least where there is no interaction between the aerogel and the electronics. Sol-Gel Science by C.J. Brinker and G.W. Scherer describes several of these uses in chapter 14. These passive uses may partially include some types of optical coatings, some types of protective coatings, and some types of porous coatings.

Antireflective (AR) coatings can require a wide range of porosities. These will typically range from 20% porous to 70% porous, although higher porosities (above 90%) may be useful where there is adequate surface protection, and lower porosities (down to 10%, or below) may be useful in high performance coatings or coatings on substrates with a high index of refraction. In some single layer AR coatings, it may be preferable to use gels with porosities between 30% and 55%. Higher performance, multi-layer AR coatings will prefer denser layers (e.g., porosity between 10% and 30%) next to the substrate, and less dense layers (e.g., porosity between 45% and 90%) next to the air interface. For higher strength/toughness applications, especially where high strength and surface area are the primary goals, it may be preferable to use a low porosity gel with a porosity between 20% to 40%. Other thin film coatings may need the lowest density practical, thus needing porosities greater than 85%, 90%, or even 95%.

There are also many bulk gel applications that can benefit from these new high strength, easy to fabricate aerogels. These bulk gel uses include (but are not limited to) nanoporous (e.g., molecular) sieves, thermal insulation, catalyst supports, adsorbents, acoustic insulation, and optiseparation membranes. As a general rule, many bulk uses prefer porosities greater than 60%, with critical applications preferring porosities greater than 80% or 90%. However, structural strength and integrity considerations may limit the practical porosity to no more than 95%. Some applications, possibly including sieves, may need to sacrifice some porosity for higher strength and stiffness. These higher stiffness requirements may require dielectrics with porosities as low as 30 or 45%. In other high strength/toughness applications, possibly including catalyst supports and sensors, where surface area may be more important than density, it may be preferable to use a low porosity gel with a porosity between 20% and 40%.

Typical sol-gel thin film processes produce gels which collapse and densify upon drying, thus forming xerogels having limited porosity (Up to 60% with large pore sizes, but generally substantially less than 50% with pore sizes of interest). Under the uncontrolled drying conditions of xerogel film formation, many of the internal pores permanently collapse. However, in thin film aerogel formation, the pores remain substantially uncollapsed, even though there may be a small amount of shrinkage during aging and/or drying that affects the final density.

Referring now to Figure 12A, a semiconductor substrate 10 (typically in wafer form) is shown. Common substrates include silicon, germanium, and gallium arsenide, and the substrate may include active devices, lower level wiring and insulation layers, and many other common structures not shown but known to those skilled in the art. Several patterned conductors 12 (e.g., of an Al-0.5%Cu composition)

are shown on substrate 10. Conductors 12 typically run parallel for at least part of their length, such that they are separated by gaps 13 of a predetermined width (typically a fraction of a micron). Both the conductors and gaps may have height-to-width ratios much greater than shown, with larger ratios typically found in devices with smaller feature sizes.

In accordance with a first embodiment of the present invention, mix 61.0 mL tetraethoxysilane (TEOS), 61.0 mL glycerol, 4.87 mL water, and .2 mL 1M HNO3)) and reflux for 1.5 hours at (equivalent to) 60 (degree)C to form a stock solution. Equivalently, mix .27 mol TEOS, .84 mol glycerol, .27 mol water, and 2.04E-4 mol HNO3)) and reflux for 1.5 hours at (equivalent to) 60(degree)C. After the stock solution is allowed to cool, the solution may be diluted with ethanol to reduce the viscosity. One suitable stock solution:solvent volume ratio is 1:8. However, this ratio will depend upon desired film thickness, spin speed, and substrate. This is mixed vigorously and typically stored in a refrigerator at (equivalent to) 7(degree)C to maintain stability until use. The solution is typically warmed to room temperature prior to film deposition. 3-5 mL of this precursor sol may be dispensed at room temperature onto substrate 10, which is then spun at 1500 to 5000 rpm (depending on desired film thickness) for about 5-10 seconds to form sol thin film 14. The deposition can be performed in an atmosphere that has no special control of solvent saturation (e.g., in a cleanroom with non-exotic humidity controls). During and after this deposition and spinning, the ethanol, water, and the nitric acid are evaporating from film 14, but due to glycerol's low volatility, no substantial evaporation of the glycerol is occurring. This evaporation temporarily cools the thin film, although the film temperature rises within seconds after the evaporation rate drops off. This cooling retards, but does not prevent gelation. This evaporation also shrinks thin film 14 and concentrates the silica content of the sol, forming reduced thickness film 18. Figure 12B shows a reduced thickness sol film 18 obtained after substantially all (about 95% or more) of the ethanol has been removed. This concentrating, evaporative basification, and/or rewarming of the film typically cause gelation within seconds.

Film 18 has an approximately known ratio of silicon to pore fluid at the gel point. This ratio is approximately equal to the ratio of TEOS to glycerol in the as-deposited sol (with minor changes due to remaining water, continued reactions and incidental evaporation). As this method largely prevents the gel from permanently collapsing, this ratio determines the density of the aerogel film that will be produced from the sol thin film.

After gelation, the thin film wet gel 18 comprises a porous solid and a pore fluid, and can preferably be allowed time to age at one or more controlled temperatures, e.g., about a day at room temperature. It should be noted that the pore fluid changes somewhat during processing. These changes may be due to continued reactions, evaporation/condensation, or chemical additions to the thin film. Aging may preferably be accomplished by letting the substrate and gel sit for approximately 24 hours at about 25 (degree) C or by heating it to 130-150(degree) C for about 1 minute in a closed container.

Aged film 18 may be dried without substantial densification by one of several methods. However, with these new glycerol-based gels, one alternative is to use a solvent exchange to replace the aging fluid with a drying fluid and then air dry the film 18 from this drying fluid. This drying method uses a solvent exchange to replace the aging fluid with a different fluid. Whether this fluid is identical to the aging fluid or not, the pore fluid that is present during drying is sometimes referred to as "drying fluid". If used, the solvent exchange replaces the aging fluid that is dominated by the glycerol and its associated high surface tension with a drying fluid that has a lower surface tension. This solvent exchange may be carried out as a one or two step process. In the two step process, the first step replaces the aging fluid with an intermediate by dispensing approximately 3-8 mL of ethanol at room temperature (or warmer) onto aged thin film 18, then spinning the wafer between approximately 50 and 500 rpm for about 5-10 seconds. It sometimes requires between 3 and 6 spin-on sequences to replace most of the aging fluid. The second step preferably replaces the intermediate fluid with a drying fluid such as heptane. This step

preferably comprises dispensing approximately 3-8 mL of heptane at room temperature (or warmer) onto aged thin film 18, then spinning the wafer between approximately 50 and 500 rpm for about 5-10 seconds. It sometimes requires between 3 and 6 spin-on sequences to replace most of the intermediate fluid. This solvent exchange method allows us to remove nearly all the glycerol-containing fluid before drying. The drying fluid (heptane in this case) is finally allowed to evaporate from the wet gel 18, forming a dry nanoporous dielectric (dried gel). If the film can be satisfactorily dried from a liquid that is soluble with the aging fluid, the intermediate may not be required. In many cases, the wet gel can be dried directly from ethanol, or other suitable solvent.

This evaporation may be performed by exposing the wafer surface to an atmosphere that is not near saturated with the drying fluid. For example, the wafer could be in a substantially uncontrolled atmosphere, or a drying gas could be introduced into the atmosphere. To prevent boiling, drying should preferably start at a temperature somewhat below the boiling point of the drying fluid, such as room temperature. If a higher boiling point drying fluid, such as glycerol, is used (e.g., drying without solvent replacement), the starting drying temperature can be increased to a temperature near or equal to the aging temperature. As the thin film becomes predominately dry (typically within seconds), the temperature should then be increased above the boiling point of both the aging fluid and the drying fluid. This method prevents destructive boiling, yet insures that all fluid is removed. Glycerol, as well as some other fluids, either decompose at approximately the same temperature as they boil, or decompose in lieu of boiling. With these fluids, particularly fluids like glycerol that can decompose into toxic substances, care should be taken not to overheat the evaporated fluid or the undried wafer. After drying, it is preferable to bake the nanoporous dielectric for a short time (such as 300(degree) for 15 to 60 minutes) to help remove any residual materials, such as organics, that are in or on the dielectric. The theoretical dielectric constant (before surface modification) of this embodiment is 1.3.

In order to reduce the dielectric constant, it is preferable to dehydroxylate (anneal) the dried gel. This may be done by placing the wafer in a dry atmosphere with an agent, such as hexamethyldisilazane (HMDS) or hexaphenyldisilazane vapor. The HMDS will replace much of the water and/or hydroxyls bound to the dried gel's pore surfaces with methyl groups. This replacement may be performed at room temperature, or warmer. This replacement can not only remove water and/or hydroxyls, it can also render the dried gel hydrophobic (water repelling). The hexaphenyldisilazane will also remove water and/or hydroxyls and render the dried gel hydrophobic. However, the phenyl groups have a higher temperature stability than the methyl groups, at the expense of a slightly higher dielectric constant.

Figure 13 contains a flow chart of a general method for obtaining an aerogel thin film from a precursor sol according to one embodiment of the present invention. Table 3 is a quick summary of some of the substances used in this method.

In accordance with a second, higher density, embodiment of the present invention, mix 150.0 mL TEOS, 61.0 mL glycerol, 150.0 mL ethanol, 12.1 mL water, and .48 mL 1M HNO3)) and reflux for 1.5 hours at (equivalent to) 60(degree)C to form a stock solution. Equivalently, mix .67 mol TEOS, .84 mol glycerol, 2.57 mol ethanol, .67 mol water, and 4.90E-4 mol HNO3)) and reflux for 1.5 hours at (equivalent to) 60 (degree)C. After the stock solution is allowed to cool, the solution may be diluted with ethanol to reduce the viscosity. One suitable stock solution:solvent volume ratio is 1:8. This is mixed vigorously and typically stored in a refrigerator at (equivalent to) 7(degree)C to maintain stability until use. The solution is warmed to room temperature prior to film deposition. 3-5 mL of this precursor sol may be dispensed at room temperature onto substrate 10, which is then spun at 1500 to 5000 rpm (depending on desired film thickness) for about 5-10 seconds to form sol thin film 14. The deposition can be performed in an atmosphere that is not solvent controlled (e.g., standard exhausts in a cleanroom with non-exotic humidity controls). During and after this deposition and spinning, ethanol (a viscosity reduction additive and a reaction product from the TEOS and water) and water is evaporating from film 14, but due to

glycerol's low volatility, no substantial evaporation of the glycerol is occurring. This evaporation shrinks thin film 14 and concentrates the silica content of the sol forming reduced thickness film 18. Figure 12B shows a reduced thickness sol film 18 obtained after substantially all (about 95% or more) of the water has been removed. This concentrating typically causes gelation within minutes.

Further processing generally follows the process described in the first embodiment. After gelation, the thin film wet gel 18 comprises a porous solid and a pore fluid, and can preferably be allowed time to age at one or more controlled temperatures. Aged film 18 may be dried without substantial densification by one of several methods. However, with the lower density formulations of these new glycerol-based gels, it is preferable to perform a non-supercritical drying, such as a solvent exchange followed by air drying the film 18 from the drying fluid, as described in the first embodiment. The nanoporous dielectric can then be subjected to a post-dry bake and/or a surface modification, as described in the first embodiment. The theoretical dielectric constant (before surface modification) of this embodiment is 1.6.

In accordance with a third, higher density, embodiment of the present invention, mix 208.0 mL TEOS, 61.0 mL glycerol, 208.0 mL ethanol, 16.8 mL water, and .67 mL 1M HNO3)) and reflux for 1.5 hours at (equivalent to) 60(degree)C to form a stock solution. Equivalently, mix .93 mol TEOS, .84 mol glycerol, 3.56 mol ethanol, .93 mol water, and 6.80E-4 mol HNO3)) and reflux for 1.5 hours at (equivalent to) 60 (degree)C. After the stock solution is allowed to cool, the solution may be diluted with ethanol to reduce the viscosity. One suitable stock solution:solvent volume ratio is 1:8. This is mixed vigorously and typically stored in a refrigerator at (equivalent to) 7(degree)C to maintain stability until use. The solution is warmed to room temperature prior to film deposition. 3-5 mL of this precursor sol may be dispensed at room temperature onto substrate 10, which is then spun at 1500 to 5000 rpm (depending on desired film thickness) for about 5-10 seconds to form sol thin film 14. The deposition can be performed in an atmosphere that is not solvent controlled (e.g., standard exhausts in a cleanroom with non-exotic humidity controls). During and after this deposition and spinning, ethanol and water is evaporating from film 14, but due to glycerol's low volatility, no substantial evaporation of the glycerol is occurring. This evaporation shrinks thin film 14 and concentrates the silica content of the sol forming reduced thickness film 18. Figure 12B shows a reduced thickness sol film 18 obtained after substantially all (about 95% or more) of the water has been removed. This concentrating typically causes gelation within minutes.

Further processing generally follows the process described in the first embodiment. After gelation, the thin film wet gel 18 comprises a porous solid and a pore fluid, and can preferably be allowed time to age at one or more controlled temperatures. Aging may be accomplishedby letting the device sit for approximately 24 hours at 25(degree) C. Aged film 18 may be dried without substantial densification by one of several methods, a solvent exchange followed by air drying. However, especially in this higher density formulation of these new glycerol-based gels, it is preferable to air dry the film 18 from the aging fluid. In this direct drying method, the wafer surface is exposed to an atmosphere that is not near saturated with the drying fluid. A simple method is to remove the cover from a low volume aging chamber, thus exposing the gel surface to a substantially uncontrolled atmosphere. Another method introduces a drying gas into the aging chamber or atmosphere. With this direct drying method, the starting drying temperature can preferably be increased to a temperature near or equal to the aging temperature. This high temperature drying reduces surface tension and associated shrinkage, speeds drying, and simplifies processing. As the thin film becomes predominately dry (typically within seconds for high temperature drying), the temperature should then be increased above the boiling point of both the aging fluid and the drying fluid (they are often the same fluid). This method prevents destructive boiling, yet insures that all fluid is removed. Since this method's drying fluid comprises glycerol, which can decompose into toxic substances, care should be taken not to overheat the evaporated fluid or the undried wafer. The nanoporous dielectric can then be subjected to a post-dry bake and/or a surface modification, as described in the first embodiment. The theoretical dielectric constant (before surface modification) of this embodiment is 1.76.

In accordance with a fourth embodiment of the present invention, mix 278.0 mL TEOS, 61.0 mL glycerol, 278.0 mL ethanol, 22.5 mL water, and .90 mL 1M HNO3)) and reflux for 1.5 hours at (equivalent to) 60(degree)C to form a stock solution. Equivalently, mix 1.25 mol TEOS, .84 mol glycerol, 4.76 mol ethanol, 1.25 mol water, and 9.1E-4 mol HNO3)) and reflux for 1.5 hours at (equivalent to) 60(degree)C. After the stock solution is allowed to cool, the solution may be diluted with ethanol to reduce the viscosity. One suitable stock solution:solvent volume ratio is 1:8. This is mixed vigorously and typically stored in a refrigerator at (equivalent to) 7(degree)C to maintain stability until use. The solution is warmed to room temperature prior to film deposition. 3-5 mL of this precursor sol may be dispensed at room temperature onto substrate 10, which is then spun at 1500 to 5000 rpm (depending on desired film thickness) for about 5-10 seconds to form sol thin film 14. The deposition can be performed in an atmosphere that is not solvent controlled (e.g., standard exhausts in a cleanroom with non-exotic humidity controls). During and after this deposition and spinning, ethanol and water is evaporating from film 14, but due to glycerol's low volatility, no substantial evaporation of the glycerol is occurring. This evaporation shrinks thin film 14 and concentrates the silica content of the sol forming reduced thickness film 18. Figure 12B shows a reduced thickness sol film 18 obtained after substantially all (about 95% or more) of the water has been removed. This concentrating typically causes gelation within minutes.

Further processing generally follows the process described in the third embodiment. After gelation, the thin film wet gel 18 comprises a porous solid and a pore fluid, and can preferably be allowed time to age at one or more controlled temperatures. Aged film 18 may be dried without substantial densification by one of several methods. However, it is preferable to air dry the film 18 from the aging fluid, as described in the third embodiment. The nanoporous dielectric can then be subjected to a post-dry bake and/or a surface modification, as described in the first embodiment. The theoretical dielectric constant (before surface modification) of this embodiment is 1.96.

In accordance with a fifth embodiment of the present invention, mix 609.0 mL TEOS, 61.0 mL glycerol, 609.0 mL ethanol, 49.2 mL water, and 1.97 mL 1M HNO3)) and reflux for 1.5 hours at (equivalent to) 60(degree)C to form a stock solution. Equivalently, mix 2.73 mol TEOS, .84 mol glycerol, 10.4 mol ethanol, 2.73 mol water, and 2.00E-3 mol HNO3)) and reflux for 1.5 hours at (equivalent to) 60(degree) C. After the stock solution is allowed to cool, the solution may be diluted with ethanol to reduce the viscosity. One suitable stock solution:solvent volume ratio is 1:8. This is mixed vigorously and typically stored in a refrigerator at (equivalent to) 7(degree)C to maintain stability until use. The solution is warmed to room temperature prior to film deposition. 3-5 mL of this precursor sol may be dispensed at room temperature onto substrate 10, which is then spun at 1500 to 5000 rpm (depending on desired film thickness) for about 5-10 seconds to form sol thin film 14. The deposition can be performed in an atmosphere that is not solvent controlled (e.g., standard exhausts in a cleanroom with non-exotic humidity controls). During and after this deposition and spinning, ethanol and water is evaporating from film 14, but due to glycerol's low volatility, no substantial evaporation of the glycerol is occurring. This evaporation shrinks thin film 14 and concentrates the silica content of the sol forming reduced thickness film 18. Figure 12B shows a reduced thickness sol film 18 obtained after substantially all (about 95% or more) of the water has been removed. This concentrating typically causes gelation within minutes.

Further processing generally follows the process described in the third embodiment. After gelation, the thin film wet gel 18 comprises a porous solid and a pore fluid, and can preferably be allowed time to age at one or more controlled temperatures. Aged film 18 may be dried without substantial densification by one of several methods. However, it is preferable to air dry the film 18 from the aging fluid, as described in the third embodiment. The nanoporous dielectric can then be subjected to a post-dry bake and/or a surface modification, as described in the first embodiment. The theoretical dielectric constant (before surface modification) of this embodiment is 2.5.

Other ratios of solvent to reactant ratios can be used to provide different porosities/dielectric constants. Figure 14 shows the theoretical relationship between the molar ratio of glycerol molecules to metal atoms and the porosity of a nanoporous dielectric for the case where all ethanol is evaporated from the deposited sol. Typically, the higher porosity glycerol-based gels (generally less than about .51 g/cc) prefer a solvent exchange or other method to lessen shrinkage during drying. On the other hand, the lower porosity gels require care to prevent early gelation. This may comprise pH adjustment, temperature control, or other methods known in the art. In some applications, it is also permissible to allow high volatility solvent evaporation after gelation.

As described above, the higher density glycerol-based gels (generally greater than about .64 g/cc) can be aged and dried with little shrinkage, even without a solvent exchange. An unaged wafer may be placed in a small volume furnace, or a small container, which can go on a hot plate. After an optional evacuation, the container is sealed at room temperature. The container remains sealed as the temperature is ramped up, quickly aging the film, and lowering the aging/drying fluid viscosity. After sufficient aging (possibly during the temperature ramp), the gel is ready for drying. At temperatures near glycerol's boiling point, the glycerol viscosity can be low enough (compared to the strength of an aged film of the predetermined porosity), that the glycerol in the furnace atmosphere can be removed and the film directly dried. Note that, in the most demanding low density applications, a somewhat lower surface tension can be obtained by increasing the drying temperature above the boiling point of glycerol. In these cases, the furnace needs to withstand the pressure (most sub-critical drying situations can be handled with pressures under 1 to 3 MPa). Additionally, care needs to be taken that the glycerol in the furnace atmosphere is, especially at first, slowly removed. The glycerol in the furnace atmosphere may be removed, e.g., by bleeding off the pressure, by a vacuum pump, or by sweeping the glycerol off with a gas. The furnace temperature may be held constant or continue to be raised while the glycerol is being removed (the furnace may be ramped on up to the bake temperature while sweeping the glycerol off with the gas). While some glycerol can be introduced during heating to minimize evaporation from the film, preferably the furnace volume is low enough that evaporation does not significantly reduce film thickness even without the introduction of glycerol during heating. If a film requires supercritical drying, perhaps to eliminate even temporary shrinkage, it is preferable to use a CO2)) solvent exchange as is well known in the art.

Although the same stock solutions can be used for bulk aerogels as thin film aerogels, the processing is substantially different. With different stock solution mixtures, the following example can be adapted to provide bulk gels with different porosities. In accordance with a bulk aerogel embodiment of the present invention, mix 208.0 mL TEOS, 61.0 mL glycerol, 208.0 mL ethanol, 16.8 mL water, and .67 mL 1M HNO3)) and reflux for 1.5 hours at (equivalent to) 60(degree)C to form a stock solution. Equivalently, mix .93 mol TEOS, .84 mol glycerol, 3.56 mol ethanol, .93 mol water, and 6.80E-4 mol HNO3)) and reflux for 1.5 hours at (equivalent to) 60(degree)C. This is typically stored in a refrigerator at (equivalent to) 7(degree)C to maintain stability until use. The stock solution is preferably warmed to room temperature prior to placing into molds. After pouring into molds, the ethanol, water, and acid is allowed to evaporate, but due to glycerol's low volatility, no substantial evaporation of the glycerol is occurring. This evaporation reduces the volume of the stock solution precursor sol and concentrates the silica content of the sol. It is allowable for at least some of the evaporation to occur before filling the mold. This pre-fill evaporation might be especially useful if the configuration of the mold does not lend itself to substantial evaporation after filling, such as a low exposed surface area mold or a mold configuration that is incompatible with shrinkage. Although this evaporation is not required, it has several advantages, including faster gelation without a catalyst and less shrinkage after gelation.

After this evaporation, the sol has an approximately known ratio of silicon to pore fluid at the gel point. This ratio is approximately equal to the ratio of TEOS to glycerol in the precursor mix (with minor changes due to remaining water, continued reactions and incidental evaporation). As this method largely

prevents the gel from permanently collapsing, this ratio determines the density of the aerogel that will be produced. If the sol does not gel during evaporation, this sol will gel soon after substantially all of the water, ethanol, and acid has evaporated.

Alternatively, one may catalyze the precursor with .5M ammonium nitrate before filling the mold. With this mixture, the sol typically gels in minutes. Remove the wet gel from the mold and allow the ethanol and water to evaporate. Typically, the gel will shrink during this evaporation. However, as with the other approaches, when the evaporation is substantially complete, the sol has an approximately known ratio of silicon to pore fluid at the gel point. This ratio is approximately equal to the ratio of TEOS to glycerol in the precursor mix (with minor changes due to remaining water, continued reactions and incidental evaporation). As this method largely prevents the gel from permanently collapsing, this ratio determines the density of the aerogel that will be produced.

After gelation, the wet gel comprises a porous solid and a pore fluid, and can preferably be allowed time to age at one or more controlled temperatures. Aging may preferably be accomplished by letting the substrate and gel sit for approximately 24 hours at about 25(degree) C or by heating it to 130-150 (degree) C for about 5 minutes in a closed container. These high temperature aging parameters are valid for a 5 mm diameter bulk aerogel. However, due to the wet gel's low thermal conductivity, the high temperature accelerated aging time and temperature combinations are highly dependent upon the configuration of the bulk gel.

After this initial aging, remove the gel from the molds and dry directly from the mother liquor (that is, the pore fluid remaining at the end of aging, with no solvent exchanges for aging or drying). A slow ramp to and hold at about 500(degree) C will dry the gel.

Instead of drying directly from the mother liquor, it may be preferable, particularly with higher porosity gels, to perform a solvent exchange. This solvent exchange may be carried out as a one or two step process. The first step replaces the aging fluid with an intermediate and the second step preferably replaces the intermediate fluid with a low surface tension drying fluid such as heptane. In this method, It is preferable to remove the gels from the molds and place it in sealed tubes containing ethanol and allow a pore fluid exchange for 8 hours at 50 degrees C. At the end of a 8 hour interval, rinse the gels with ethanol and then store in fresh ethanol in an oven at 50 degrees C. After three to six such intervals, replace the ethanol with hexane in a similar manner. This solvent exchange method allows us to remove nearly all the glycerol-containing fluid before drying. The drying fluid (heptane in this case) is finally allowed to evaporate from the wet gel, forming a dry aerogel. If the film can be satisfactorily dried from a liquid that is soluble with the aging fluid, the intermediate may not be required. In many cases, the wet gel can be dried directly from ethanol, or other suitable solvent.

After drying, it is often preferable to bake the aerogel for a short time (such as 300(degree) for 15 to 60 minutes) to help remove any residual materials, such as organics, that are in or on the aerogel. In some applications, it is also desirable to dehydroxylate (anneal) the dried gel. This may be done by placing the dry aerogel in a dry atmosphere comprising a surface modification agent, such as trimethylchlorosilane (TMCS), hexamethyldisilazane (HMDS), or hexaphenyldisilazane vapor. The HMDS will replace much of the water and/or hydroxyls bound to the dried gel's pore surfaces with methyl groups. This replacement can be performed at room temperature, or warmer. This replacement can not only remove water and/or hydroxyls, it can also render the dried gel hydrophobic (water repelling). The hexaphenyldisilazane will also remove water and/or hydroxyls and render the dried gel hydrophobic. However, the phenyl groups have a higher temperature stability than the methyl groups.

In accordance with an ethylene glycol-based embodiment of the present invention, mix tetraethoxysilane (TEOS), ethylene glycol, ethanol, water, and acid (1M HNO3))) in a molar ratio of 1 : : 2.4 : 1.5 : 1 :

0.042 and reflux for 1.5 hours at (equivalent to) 60(degree)C. After the mixture is allowed to cool, the solution is diluted down with ethanol to a composition of 70% (by volume) original stock solution and 30% (by volume) ethanol. This is mixed vigorously and typically stored in a refrigerator at (equivalent to) 7(degree)C to maintain stability until use. The solution is warmed to room temperature prior to film deposition. A mixture of stock solution and 0.25M NH4))OH catalyst (10:1 volume ratio) is combined and mixed. 3-5 mL of this precursor sol may be dispensed at room temperature onto substrate 10, which is then spun at 1500 to 5000 rpm (depending on desired film thickness) for about 5-10 seconds to form sol thin film 14. The deposition can be performed in an atmosphere that is uncontrolled. However, it is preferable to deposit and gel the sol in a clean room with standard humidity controls. During and after this deposition and spinning, the ethanol/water mixture is evaporating from film 14, but due to ethylene glycol's low volatility, no substantial evaporation of the ethylene glycol is occurring. This evaporation shrinks thin film 14 and concentrates the silica content of the sol forming reduced thickness film 18. Figure 12B shows a reduced thickness sol film 18 obtained after substantially all (about 95% or more) of the ethanol has been removed. This concentrating, combined with the catalyst, typically causes gelation within minutes or seconds.

Film 18 has an approximately known ratio of silicon to pore fluid at the gel point. This ratio is approximately equal to the ratio of TEOS to ethylene glycol in the as-deposited sol (with minor changes due to remaining water, continued reactions and incidental evaporation) . To the extent that the gel is prevented from collapsing, this ratio will determine the density of the aerogel film that will be produced from the sol thin film.

After gelation, the thin film wet gel 18 comprises a porous solid and a pore fluid, and can preferably be allowed time to age at one or more controlled temperatures, e.g., about a day at room temperature. It should be noted that the pore fluid changes somewhat during processing. These changes may be due to continued reactions and/or evaporation/condensation. Aging may preferably be accomplished by letting the device sit in a low volume aging chamber for approximately 5 minutes at about 100 degrees C.

Aged film 18 may be dried without substantial densification by one of several methods, a solvent exchange followed by air drying. However, it is preferable to air dry the film 18 from the aging fluid, as described in the third glycerol embodiment. The nanoporous dielectric can then be subjected to a post-dry bake and/or a surface modification, as described in the first glycerol embodiment.

In accordance with another ethylene glycol-based embodiment of the present invention, mix tetraethoxysilane (TEOS), ethylene glycol, water, and acid (1M HNO3))) in a molar ratio of 1 : 4 : 1 : 0.042 and reflux for 1.5 hours at (equivalent to) 60(degree)C. This is typically stored in a refrigerator at (equivalent to) 7(degree)C to maintain stability until use. The solution is preferably warmed to room temperature prior to film deposition. 3-5 mL of this precursor sol may be dispensed (without catalyst) at room temperature onto substrate 10, which is then spun at 1500 to 5000 rpm (depending on desired film thickness) for about 5-10 seconds to form sol thin film 14. The deposition can be performed in an atmosphere that is uncontrolled. However, it is preferable to deposit and gel the sol in a clean room with standard humidity controls. During and after this deposition and spinning, ethanol and water is evaporating from film 14, but due to ethylene glycol's low volatility, no substantial evaporation of the ethylene glycol is occurring. This evaporation shrinks thin film 14 and concentrates the silica content of the sol forming reduced thickness film 18. Figure 12B shows a reduced thickness sol film 18 obtained after substantially all (about 95% or more) of the water has been removed. This concentrating typically causes gelation within minutes.

After gelation, the thin film wet gel 18 comprises a porous solid and a pore fluid, and can preferably be allowed time to age at one or more controlled temperatures, e.g., about a day at room temperature. It should be noted that the pore fluid changes somewhat during processing. Aging may preferably be

accomplished by letting the device sit in a low volume aging chamber for approximately 5 minutes at about 100 degrees C.

Aged film 18 may be dried without substantial densification by one of several methods, including a solvent exchange followed by air drying. However, it is preferable to air dry the film 18 from the aging fluid, as described in the third glycerol embodiment. The nanoporous dielectric can then be subjected to a post-dry bake and/or a surface modification, as described in the first glycerol embodiment.

The discussion to this point has shown some of the advantages of aging in a closed container. Since suitable aging chambers do not seem to exist, we will describe the chambers we have invented to implement this process. One embodiment of aging container is illustrated in Figures 16A, 16B and 16C. In this embodiment, a processing apparatus comprises a body 20, having a substantially planar plate 22 with a resilient seal 24 attached thereto. Plate 22 need only be planar to the extent necessary to provide clearance with a thin film during operation, and may be constructed of any material compatible with the underlying process (e.g., semiconductor fabrication), although materials with high thermal conductivity, such as stainless steel, glass, or aluminum are preferred. Resilient seal 24 should preferably be designed to withstand wet gel processing temperatures and pore fluids; many suitable materials, including TEFLON- and neoprene-based materials, are known to those of ordinary skill in the art. Depending on the nature of temperature control used in the apparatus, it may be preferable to have seal 24 be either substantially thermally insulating or thermally conductive.

In operation, body 20 may simply be rested on a substrate 26, as shown in Figure 16C. This substrate may be an optical substrate, such as glass or plastic, or a semiconductor substrate, such as a Si wafer. In this embodiment, seal 24 functions both as an atmospheric seal and as a spacer which sets the volume of chamber 32 formed by substrate surface 28, chamber surface 30 and seal 24. For example, seal 24 may be designed to compress to a thickness of about 1 mm under the weight of plate 22, thus creating chamber 32 with a 1 mm height when body 20 is placed on substrate 26. For many thin film applications, chamber 32 need only be substantially sealed, as some small degree of vapor leakage over the course of processing substrate 26 will not appreciably affect the final film properties.

Body 20 finds application at many points in an aerogel thin film process. It may be used to limit evaporation before a sol film has gelled, as an aging chamber for wet gel thin films, as a storage or transport chamber for such films, or as a drying chamber. In all of these applications, it is recognized that both sol and gel thin films contain extremely small amounts of liquid, such that a chamber of limited volume is necessary to prevent substantial evaporation from the film.

In another embodiment, body 20 may comprise more elements, as shown in Figures 17A and 17B. In this embodiment, body 20 additionally comprises a substrate holder 36 and substrate temperature control means 34. This embodiment shows the additional aspect of a seal 24 located outboard of the substrate (or in some cases seal 24 may even be deleted), such that a thin film may be formed on the entirety of substrate surface 28. When chamber 32 is closed, planar plate 22 and wafer holder 36 may be thermally coupled such that temperature control means 34 may be used to simultaneously regulate the temperature of body 20, substrate 26 and chamber 32.

In another embodiment shown in Figures 18A and 18B, seal 24 provides some degree of thermal isolation between planar plate 22 and wafer holder 36. This allows temperature control means 34 to control substrate temperature, while separate temperature control means 38 are used to control planar plate temperature. Such an embodiment may have an advantage for drying a wet gel film, as the temperature of planar plate 22 can be selectively lowered to promote condensation on chamber surface 30.

Figures 19A, 19B and 19C show additional aspects of these aging chambers. For example, in Figure 19A, substrate 26 is shown being processed in an inverted position. In this embodiment, accidental or purposeful condensation onto chamber surface 30 may be collected without the possibility of such condensation dropping onto substrate surface 26. In Figure 19B, not only is substrate 26 processed inverted, but a first solvent layer 42 (preferably of the same composition as at least one pore fluid) is dispensed, e.g., from a first solvent supply tube 40, onto chamber surface 30 prior to closing the chamber. In this embodiment, layer 42 may be used to help saturate the processing atmosphere, resulting in less evaporation of pore fluid from substrate 26.

In Figure 19C, an embodiment is shown wherein some atmospheric adjustment means 44 is connected through at least one port 46 (which may be closeable) to chamber 32. Atmospheric adjustment means 44 may be used to create a vacuum or to overpressure chamber 32 as appropriate, or to exchange the atmosphere in chamber 32, or to supply a pore fluid vapor to chamber 32. This embodiment may be used, for example, to age a thin film at a temperature higher than the boiling point of a pore fluid, by operating chamber 32 at above atmospheric pressure. This embodiment may also be used to remove at least a portion of the pore fluid vapor from chamber 32 after aging, thereby allowing the thin film to dry.

Although this invention has been described in terms of several embodiments, many of these steps may be modified within the scope of the invention, and other steps can be included to enhance the overall process. For example, the initial thin film may be deposited by other common methods, such as dip-coating, flow coating, or spray-coating instead of spin-coating. Likewise, the solvent exchange may use dip coating, spray coating, or immersion in a liquid or vaporous solvent instead of spin-coating. When using a vaporous solvent, the wafer may be cooled to a temperature lower than the atmosphere, thus promoting condensation on the wafer. While water might otherwise be considered a solvent in such a process, for discussion purposes in this application, water is not considered a solvent.

Although both glycerol and ethylene glycol each have unique advantages, there are other low volatility solvents that can be useful in low shrinkage nanoporous dielectric fabrication. Although it is preferable to analyze a solvent to determine its expected evaporation rate, a preliminary preference on the selection of the low volatility solvent can be made. Nearly all solvents that have a low evaporation rate at room temperature will have a boiling point greater than 140(degree) C. Although some solvents with boiling points less than 140(degree) C may be useful, a preferred evaporation rate will typically be found with solvents that have a boiling point greater than 160(degree) C, and more preferably greater than 190 (degree) C. Solvents with boiling points greater than 230(degree) C may also have low enough evaporation rates to be suitable for deposition and/or aging with little atmospheric control for short periods of time at 40-80(degree) C. For processing at 100-150(degree) C with little atmospheric control, it is preferable to use solvents with boiling points greater than 270(degree) C. This gives some rough preferences on the lower limit of preferred boiling points. There are also rough preferences on the upper limit of preferred boiling points. Most solvents with boiling points greater than 500(degree) C will be so viscous that they require extra care during processing. Typically, the more useful solvents will have boiling points less than 350(degree) C, and preferably less than 300(degree) C. If it is not convenient to dilute or heat the sol during deposition, it may even be preferable to use a low volatility solvent with a boiling point less than 250(degree) C. If no one solvent gives all the desired properties, two or more may be mixed to improve the performance. Thus, our initial preliminary preference on the selection of the low volatility solvent is a boiling point in the 175-250(degree) C range and (for TEOS based gels) that it be miscible with both water and ethanol. Based on these preliminary preferences, some suitable low volatility solvent candidates besides glycerol and ethylene glycol are 1,4-butylene glycol and 1,5-pentanediol.

If it is convenient to do the deposition and aging above room temperature, this opens up additional possibilities. One modification would be to use a solvent that is not a liquid, but a solid, at room

temperature. This allows the potential use of many more materials. Many of these higher melting point materials have even lower volatility than the low volatility "room temperature liquid solvents" (liquid solvents) have at elevated deposition and aging temperatures. Although there is no required upper melting point temperature, process simplicity indicates that these "room temperature solid solvents" (solid solvents) should have melting points less than 60 degrees C, and preferably less than 40 degrees C. An additional desirable feature for a potential solid solvent is that it readily solidify to an amorphous phase. This amorphous solidification would reduce the chance of gel damage during an accidental cooling. Additionally, this might allow the solvent to be removed by freeze drying. An alternative approach to maintaining the precursor temperature above the melting point of a solid solvent is to dissolve the solid solvent in a carrier liquid. This carrier liquid can be water, alcohol, or any other liquid typically used in thin film aerogel/xerogel processing. The carrier liquid could also be a compatible liquid introduced only as a carrier.

The surprisingly good behavior of glycerol and ethylene glycol give some clues to other preferred solvents. We have identified several solvents that may give properties slightly different than either ethylene glycol or glycerol, yet still retain many of their advantages. The most promising additional solvents include 1,2,4-butanetriol; 1,2,3- butanetriol; 2 methyl-propanetriol; and 2-(hydroxymethyl)-1,3-propanediol; 1-4, 1-4, butanediol; and 2-methyl-1,3-propanediol. Other potential solvents include the polyols, either alone or in combination with ethylene glycol, glycerol, or other solvents.

This use of a low volatility solvent allows a loosening of the required atmospheric control during deposition, gelation, and/or aging. This is because, that even though saturation should still preferably be avoided, the atmospheric solvent concentration can be lowered without excessive evaporation. This wider concentration window can be used to allow wider variations in temperature across the deposition chamber (especially near the wafer and any evaporative cooling effects). An initial goal is to allow at least a 1 degree C temperature variation. Thus, the vapor concentration of the low volatility solvent in the atmosphere should be such that the condensation temperature (analogous to dew point) of the solvent vapor is at least 1 degrees Celsius less than the temperature of the substrate. Actually, the critical item is the surface of the deposited sol and/or gelled sol. However, the thin film nature of the sol keeps the temperature differences between the sol and the substrate small. Since it is may be much easier to measure the substrate temperature, these two temperatures will be used interchangeably in this patent. Even though 1 degree C temperature uniformity may be obtainable under some conditions, volume production will probably require at least a 3 degree C tolerance window, and preferably a 10 degree C tolerance window. However, the ultimate goal is to deposit, gel, and age in an uncontrolled or a substantially uncontrolled atmosphere. In this most preferred approach (a substantially uncontrolled atmosphere), atmospheric controls during deposition, gelation, and aging are limited to standard cleanroom temperature and humidity controls, although the wafer and/or precursor sol may have independent temperature controls. If this substantially uncontrolled atmosphere allows excessive evaporation, then either passive or less preferably, active atmospheric controls may be needed. For the purposes of this application, passive controls are limited to the placing the wafer in a relatively small container. This container may be partially or fully sealed and may or may not also contain a liquid reservoir of the solvent. However, the container will not have exotic environmental controls for the wafer, container atmosphere, and/or reservoir.

Another example of modification to the basic method is that, before drying (and generally, but not necessarily, after aging), the thin film wet gel 18 may have its pore surfaces modified with a surface modification agent. This surface modification step replaces a substantial number of the molecules on the pore walls with those of another species. If a surface modifier is applied, it is generally preferable to remove the water from the wet gel 18 before the surface modifier is added. The water can be removed by rinsing the wafer in pure ethanol, preferably by a low speed spin coating as described in the solvent exchange in the first embodiment example. This water removal is beneficial, because water will react

with many surface modification agents, such as HMDS; however, it is not necessary. With our new glycerol-based method, surface modification need not be performed to help prevent pore collapse, but it can be used to impart other desirable properties to the dried gel. Some examples of potentially desirable properties are hydrophobicity, reduced dielectric constant, increased resistance to certain chemicals, and improved temperature stability. Some potential surface modifiers that may impart desirable properties include hexamethyldisilazane (HMDS), the alkyl chlorosilanes (trimethylchlorosilane (TMCS), dimethyldichlorosilane, etc.), the alkylalkoxysilanes (trimethylmethoxysilane, dimethyldimethoxysilane, etc.), phenyl compounds and fluorocarbon compounds. One useful phenyl compound is hexaphenyldisilazane. Some other useful phenyl compounds will typically follow the basic formula, Phx))Ay))SiB(4-x-y))), where, Ph is a phenolic group, A is a reactive group such as Cl or OCH3)), and B are the remaining ligands which, if there are two, can be the same group or different. Some examples of these phenyl surface modification agents include compounds with 1 phenolic group such as phenyltrichlorosilane, phenyltrifluorosilane, phenyltrimethoxysilane, phenyltriethoxysilane, phenylmethylchlorosilane, phenylethyldichlorosilane, phenyldimethylethoxysilane, phenyldimethylchlorosilane, phenyldichlorosilane, phenyl(3-chloropropyl)dichlorosilane, phenylmethylvinylchlorosilane, phenethyldimethylchlorosilane, phenyltrichlorosilane, phenyltrimethoxysilane, phenyltris (trimethylsiloxy) silane, and phenylallyldichlorosilane. Other examples of these phenyl surface modification agents include compounds with 2 phenolic groups such as diphenyldichlorosilane, diphenylchlorosilane, diphenylfluorosilane, diphenylmethylchlorosilane, diphenylethylchlorosilane, diphenyldimethoxysilane, diphenylmethoxysilane, diphenylethoxysilane, diphenylmethylmethoxysilane, diphenylmethylethoxysilane and diphenyldiethoxysilane. These phenyl surface modification agents also include compounds with 3 phenolic groups such as triphenylchlorosilane, triphenylflourosilane, and triphenylethoxysilane. Another important phenyl compound, 1,3-diphenyltetramethyldisilazane, is an exception to this basic formula. These lists are not exhaustive, but do convey the basic nature of the group. The useful fluorocarbon based surface modification agents include (3,3,3-trifluoropropyl)trimethoxysilane), (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1dimethylchlorsilane, and other fluorocarbon groups that have a reactive group, such as Cl or OCH3)), that will form covalent bonds with a hydroxyl group.

The paragraph above lists some of the typical useful properties for many conventional applications. However, there are other potential applications for nanoporous dielectrics and aerogels that may have different desirable properties. Examples of some other potentially desirable properties include hydrophilicity, increased electrical conductivity, increased dielectric breakdown voltage, increased or decreased reactivity with certain chemicals, and increased volatility. This list is not exhaustive. However, it shows that, depending upon the application, many different types of properties may be desirable. Thus, it is clear that many other materials that will form covalent bonds with hydroxyl groups are potential surface modifiers that may impart other potentially desirable properties.

This invention also comprises the use of gelation catalysts, such as ammonium hydroxide. This also includes the allowance of other gelation catalysts in place of the ammonium hydroxide and/or for the gelation catalyst to be added after deposition. Typically, these alternate catalysts modify the pH of the sol. It is preferable to use catalysts that raise the pH, although acid catalysts can be used. Typically, acid catalysis results in longer processing times and a denser dielectric than a base catalyzed process. Some examples of other preferred gelation catalysts include ammonia, the volatile amine species (low molecular weight amines) and volatile fluorine species. When the catalyst is added after deposition, it is preferable to add the catalyst as a vapor, mist, or other vaporish form.

This invention allows production of nanoporous dielectrics at room temperature and atmospheric pressure, without a separate surface modification step. Although not required to prevent substantial densification, this new method does not exclude the use of supercritical drying or surface modification steps prior to drying. To the extent that the freezing rates are fast enough to prevent large (e.g., 50 nm)

crystals, it is also compatible with freeze drying. In general, this new method is compatible with most prior art aerogel techniques.

Other examples of modifications involve the reaction atmosphere and/or temperature. Also coating and gelation need not be performed in the same chamber or even in the same atmosphere. For instance, the substrate may have its temperature lowered to retard gelation or elevated to speed surface modification and/or gelation. Also, total pressure and/or temperature may be varied to further control evaporation rates and/or gel time. Elevated temperature processing is typically performed at no less than 40(degree) C; however, 50(degree)C is preferred, and 70(degree)C is more preferred. When working at elevated temperatures, care should be taken (e.g., the partial pressures in the reaction atmosphere should be high enough) to prevent solvent boiling.

Although TEOS has been used as a representative example of a reactant, other metal alkoxides may be used either alone or in combination with TEOS or each other to form a silica network. These metal alkoxides include tetramethoxysilane (TMOS), methyltriethoxysilane (MTEOS), 1,2-Bis (trimethoxysilyl)ethane (BTMSE), combinations thereof, and other silicon-based metal alkoxides known in the art. A sol may also be formed from alkoxides of other metals known in the art such as aluminum and titanium. Some other precursor sols known in the art include particulate metal oxides and organic precursors. Two representative particulate metal oxides are pyrogenic (fumed) silica and colloidal silica. Some representative organic precursors are melamine, phenol furfural, and resorcinol. In addition to alternate reactants, alternate solvents may also be used. Some examples of preferred alternates for ethanol are methanol and the other higher alcohols. Other acids may be used as a precursor sol stabilizer in place of the nitric acid.

An additional modification is to allow and/or promote the formation of moderate sized (15 to 150 monomers per molecule) oligomers in the precursor sol. These larger oligomers may speed the gelation process in the deposited sol. A sol containing large oligomers may have a higher viscosity than a sol with small oligomers. However, as long as the viscosity is stable, this higher viscosity can be compensated by methods known in the art, such as adjusting solvent ratios and spin conditions. To help achieve this desired stable viscosity, the oligomerization may need to be slowed or substantially halted before deposition. Potential methods of promoting oligomerization might include heating the precursor sol, evaporating solvent, or adding small amounts of a gelation catalyst such as ammonium hydroxide. Potential methods of retarding oligomerization might include cooling the precursor sol, diluting the sol with a solvent, or restoring the precursor sol to a pH that minimizes condensation and gelation (Nitric acid could be used in conjunction with the ammonium hydroxide exemplified above).

Claims:

1. A metal-based nanoporous aerogel precursor sol, comprising

an aerogel precursor reactant, and

a first solvent comprising a polyol; wherein,

the molar ratio of said first solvent molecules to the metal atoms in said reactant is at least 1 : 16.

2. A metal-based aerogel precursor sol, comprising

an aerogel precursor reactant selected from the group consisting of metal alkoxides, at least partially hydrolyzed metal alkoxides, particulate metal oxides, and combinations thereof, and

a first solvent comprising a polyol; wherein,

the molar ratio of said first solvent molecules to the metal atoms in said reactant is at least 1 : 16.

3. The aerogel precursor sol according to Claim 2, wherein

said polyol is glycerol.

4. The aerogel precursor sol according to Claim 2, wherein

the molar ratio of said first solvent molecules to the metal atoms in said reactant is no greater than 12 : 1.

5. The aerogel precursor sol according to Claim 2, wherein

the molar ratio of said first solvent molecules to the metal atoms in said reactant is between 1 : 2 and 12 : 1.

6. The aerogel precursor sol according to Claim 2, wherein

the molar ratio of said first solvent molecules to the metal atoms in said reactant is between 1 : 4 and 4 : 1.

7. The aerogel precursor sol according to Claim 2, wherein

the molar ratio of said first solvent molecules to the metal atoms in said reactant is between 2.5 : 1 and 12 : 1.

8. The aerogel precursor sol according to Claim 2, wherein

said reactant is a metal alkoxide selected from the group consisting of tetraethoxysilane, tetramethoxysilane, methyltriethoxysilane, 1,2-Bis(trimethoxysilyl)ethane and combinations thereof.

9. The aerogel precursor sol according to Claim 2, wherein

said reactant is tetraethoxysilane.

10. The aerogel precursor sol according to Claim 9, wherein

said tetraethoxysilane is at least partially hydrolyzed.

11. The aerogel precursor sol according to Claim 2, further comprising

water.

12. The aerogel precursor sol according to Claim 2, wherein

said first solvent is ethylene glycol.

13. The aerogel precursor sol according to Claim 2, further comprising

a second solvent.

14. The aerogel precursor sol according to Claim 13, wherein said second solvent is an alcohol.

15. The aerogel precursor sol according to Claim 13, wherein said second solvent is ethanol.

16. The aerogel precursor sol according to Claim 2, further comprising a pH modification agent.

17. The aerogel precursor sol according to Claim 2, further comprising an acid.

18. The aerogel precursor sol according to Claim 17, wherein said acid is nitric acid.

19. The aerogel precursor sol according to Claim 2, wherein the pH of said sol is between 3 and 5.

20. The aerogel precursor sol according to Claim 2, further comprising a gelation catalyst.

21. The aerogel precursor sol according to Claim 20, wherein said gelation catalyst is ammonium hydroxide.

22. The aerogel precursor sol according to Claim 20, wherein the pH of said sol is between 7 and 9.

23. The aerogel precursor sol according to Claim 2, wherein the viscosity of said sol is between 1 and 12 centipoise.

24. The aerogel precursor sol according to Claim 2, wherein the viscosity of said sol is between 1 and 5 centipoise.

25. The aerogel precursor sol according to Claim 2, wherein said reactant is selected from the group consisting of pyrogenic silica, colloidal silica, and combinations thereof.

26. An aerogel precursor sol, comprising

At least partially hydrolyzed tetraethoxysilane and ethylene glycol.

27. The aerogel precursor sol according to Claim 26, wherein

the molar ratio of ethylene glycol to tetraethoxysilane is between 1 : 16 and 12 : 1.

28. A silicon-based aerogel precursor sol, comprising

a silicon based aerogel precursor, and

a first solvent comprising a polyol; wherein,

the molar ratio of said first solvent molecules to the silicon atoms in said reactant is at least 1 : 16.

29. The aerogel precursor sol according to Claim 28, wherein

the molar ratio of said first solvent molecules to the metal atoms in said reactant is no greater than 12 : 1.

30. An aerogel precursor sol, comprising

at least partially hydrolyzed tetraethoxysilane and glycerol.

31. The aerogel precursor sol according to Claim 30, wherein

the molar ratio of glycerol to tetraethoxysilane is between 1 : 16 and 12 : 1.

32. The aerogel precursor sol according to Claim 30, wherein

the molar ratio of glycerol to tetraethoxysilane is between 1 : 4 and 4 : 1.

33. A non-supercritical method of forming a nanoporous aerogel, said method comprising the steps of:

providing an aerogel precursor sol, said sol comprising an at least partially hydrolyzed metal alkoxide dispersed in a first solvent and a second solvent,

evaporating substantially all of said second solvent while preventing substantial evaporation of said first solvent, and allowing the sol to create a gel, wherein the gel comprises a porous solid and a pore fluid;

continuing to prevent substantial evaporation of said first solvent from said sol until a drying step,

wherein said drying step comprises forming a dry aerogel by removing the pore fluid in a non-supercritical drying atmosphere without substantial collapse of the porous solid;

whereby the skeletal density of the dry aerogel is determined approximately by the volume ratio of said metal alkoxide to said first solvent in said aerogel precursor sol.

34. The method of claim 33, wherein said gel is created before said evaporating step completes.

35. The method of claim 33, wherein said drying step further comprises a solvent exchange.

36. The method of claim 33, further comprising aging said gel before said drying step.

37. A non-supercritical method of forming an aerogel film on a substrate, said method comprising the steps of:

depositing a film of an aerogel precursor sol on a substrate, said sol comprising a first solvent and a second solvent;

preferentially evaporating substantially all of said second solvent from said film; and

allowing said deposited sol to cross-link to form a wet gel having pores arranged in an open-pored structure on said substrate.

38. The method of claim 37, wherein said second solvent comprises

a reaction product of said cross-linking step.

39. The method of claim 37, wherein said second solvent has a vapor pressure which is at least twice the vapor pressure of said first solvent.

40. The method of claim 37, wherein said depositing a thin film step comprises spin-coating said aerogel precursor sol onto said substrate.

41. The method of claim 37, further comprising drying said wet gel in a non-supercritical atmosphere without substantial densification of said open-pored structure.

42. The method of claim 37, wherein said wet gel is formed before said evaporating step completes.

43. The method of claim 37, further comprising aging said wet gel without substantial evaporation of said first solvent.

44. A non-supercritical method for forming a thin film aerogel on a semiconductor substrate, the method comprising the steps of:

a) providing a semiconductor substrate comprising a microelectronic circuit;

b) depositing an aerogel precursor sol upon the substrate; wherein the aerogel precursor sol comprises

a metal-based aerogel precursor reactant,

a first solvent comprising glycerol, and

a second solvent; wherein,

the molar ratio of the molecules of the glycerol to the metal atoms in the reactant is at least 1 : 16.

c) allowing the deposited sol to create a gel, wherein the gel comprises a porous solid and a pore fluid; and

d) forming a dry aerogel by removing the pore fluid in a non-supercritical drying atmosphere.

45. The method of claim 44, wherein the first solvent also comprises a polyol.

46. The method of claim 45, wherein the polyol is a glycol.

47. A non-supercritical method for forming a thin film nanoporous dielectric on a semiconductor substrate, the method comprising the steps of:

a) providing a semiconductor substrate comprising a microelectronic circuit;

b) depositing an aerogel precursor sol upon the substrate;

wherein the aerogel precursor sol comprises

a metal-based aerogel precursor reactant, and

a first solvent comprising glycerol, and

a second solvent; wherein,

the molar ratio of the molecules of the glycerol to the metal atoms in the reactant is at least 1 : 16.

c) allowing the deposited sol to create a gel, wherein the gel comprises a porous solid and a pore fluid; and

d) forming a dry, nanoporous dielectric by removing the pore fluid in a non-supercritical drying atmosphere.

48. A non-supercritical method for forming a thin film nanoporous dielectric on a semiconductor substrate, the method comprising the steps of:

a) providing a semiconductor substrate comprising a microelectronic circuit;

b) depositing an aerogel precursor sol upon the substrate;

wherein the aerogel precursor sol comprises

an aerogel precursor reactant selected from the group consisting of metal alkoxides, at least partially hydrolyzed

metal alkoxides, particulate metal oxides, and combinations thereof, and

a first solvent comprising glycerol; wherein,

the molar ratio of the molecules of the glycerol to the metal atoms in the reactant is at least 1 : 16.

c) allowing the deposited sol to create a gel, wherein the gel comprises a porous solid and a pore fluid; and

d) forming a dry, nanoporous dielectric by removing the pore fluid without substantially collapsing the porous solid;

wherein,

the forming step is performed in a drying atmosphere, and

the pressure of the drying atmosphere during the forming step is less than the critical pressure of the pore fluid.

49. The method of claim 48, wherein the molar ratio of the molecules of the glycerol to the metal atoms in the reactant is no greater than 12 : 1.

50. The method of claim 48, wherein the molar ratio of the molecules of the glycerol to the metal atoms in the reactant is between 1 : 2 and 12 : 1.

51. The method of claim 48, wherein the molar ratio of the molecules of the glycerol to the metal atoms in the reactant is between 1 : 4 and 4 : 1.

52. The method of claim 48, wherein the molar ratio of the molecules of the glycerol to the metal atoms in the reactant is between 2.5 : 1 and 12 : 1.

53. The method of claim 48, wherein the nanoporous dielectric has a porosity greater than 60% and an average pore diameter less than 20 nm.

54. The method of claim 48, wherein the nanoporous dielectric has a dielectric constant less than 2.0.

55. The method of claim 48, wherein the nanoporous dielectric has a dielectric constant less than 1.8.

56. The method of claim 48, wherein the nanoporous dielectric has a dielectric constant less than 1.4.

57. The method of claim 48, wherein the temperature of the substrate during the forming step is above the freezing temperature of the pore fluid.

58. The method of claim 48, wherein the temperature of the substrate during the forming step is above the freezing temperature of the pore fluid, and

wherein, the method does not comprise the step of adding a surface modification agent before the forming step.

59. The method of claim 48, wherein the temperature of the substrate during the forming step is above the freezing temperature of the pore fluid, and

the nanoporous dielectric has a porosity greater than 60% and an average pore diameter less than 20 nm;

wherein, the method does not comprise the step of adding a surface modification agent before the forming step.

60. The method of claim 48, further comprising the step of aging the gel.

61. The method of claim 60, wherein at least part of the aging step is performed in a substantially closed container.

62. The method of claim 60, wherein the temperature of the gel during the aging is greater than 30 degrees C.

63. The method of claim 60, wherein the temperature of the gel during the aging is greater than 80 degrees C.

64. The method of claim 60, wherein the temperature of the gel during the aging is greater than 130 degrees C.

65. The method of claim 48, wherein the porous solid has less than 2% permanent volume reduction during the pore fluid removal.

66. The method of claim 48, wherein the porous solid remains substantially uncollapsed after the pore fluid removal.

67. The method of claim 48, wherein the porous solid has less than 5% volume reduction during the pore fluid removal.

68. The method of claim 48, wherein the porous solid has less than 1% volume reduction during the pore fluid removal.

69. The method of claim 48, wherein the allowing step is performed in a gelation atmosphere, wherein the concentration of a vapor of the first solvent in the gelation atmosphere is not actively controlled.

70. The method of claim 48, wherein the allowing step is performed in a gelation atmosphere, wherein the concentration of a vapor of the first solvent in the gelation atmosphere is substantially uncontrolled.

71. The method of claim 48, wherein the reactant is a metal alkoxide selected from the group consisting of tetraethoxysilane, tetramethoxysilane, methyltriethoxysilane, 1,2-Bis(trimethoxysilyl)ethane and combinations thereof.

72. The method of claim 48, wherein the reactant is tetraethoxysilane.

73. The method of claim 48, wherein the dry, porous dielectric has a porosity greater than 60%.

74. The method of claim 48, wherein the dry, porous dielectric has a porosity between 60 % and 90%.

75. The method of claim 48, wherein the dry, porous dielectric has a porosity greater than 80%.

76. The method of claim 48, further comprising the step of replacing at least part of the pore fluid with a liquid before the removing pore fluid step.

77. The method of claim 76, wherein the liquid comprises hexanol.

78. The method of claim 48, further comprising the step of annealing the dry, porous dielectric.

79. The method of claim 48, wherein the pressure of the drying atmosphere during the forming step is

less than 3 MPa.

Claims:

1. A metal-based aerogel precursor sol, comprising an aerogel precursor reactant selected from the group consisting of metal alkoxides, at least partially hydrolyzed metal alkoxides, particulate metal oxides, and combinations thereof, and a polyol as a first solvent, the polyol being selected from the group of glycerol, ethylene glycol, 1,4-butylene glycol, 1,5-pentanediol, 1,2,4-butanetriol, 1,2,3-butanetriol, 2-methyl-propanetriol, 2-(hydroxymethyl)-1,3-propanediol, 1-4,1-4-butanediol, 2-methyl-1,3-propanediol, and combinations thereof, wherein, the molar ratio of said first solvent molecules to the metal atoms in said reactant is at least 1:16.

2. The aerogel precursor sol according to claim 1, wherein said polyol is glycerol.

3. The aerogel precursor sol according to claim 1, wherein said first solvent is ethylene glycol.

4. The aerogel precursor sol according to any of claims 1 to 3, wherein the molar ratio of said first solvent molecules to the metal atoms in said reactant is no greater than 12:1.

5. The aerogel precursor sol according to any of claims 1 to 3, wherein the molar ratio of said first solvent molecules to the metal atoms in said reactant is between 1:2 and 12:1.

6. The aerogel precursor sol according to any of claims 1 to 3, wherein the molar ratio of said first solvent molecules to the metal atoms in said reactant is between 1:4 and 4:1.

7. The aerogel precursor sol according to any of claims 1 to 3, wherein the molar ratio of said first solvent molecules to the metal atoms in said reactant is between 2.5:1 and 12:1.

8. The aerogel precursor sol according to any of claims 1 to 7, wherein said reactant is a metal alkoxide selected from the group consisting of tetraethoxysilane, tetramethoxysilane, methyl-triethoxysilane, 1,2-Bis(trimethoxysilyl)ethane and combinations thereof.

9. The aerogel precursor sol according to any of claims 1 to 7, wherein said reactant is tetraethoxysilane.

10. The aerogel precursor sol according to claim 9, wherein said tetraethoxysilane is at least partially hydrolyzed.

11. The aerogel precursor sol according to any of claims 1 to 7, wherein the metal in the aerogel precursor reactant is silicon.

12. The aerogel precursor sol according to any of claims 1 to 11, further comprising water.

13. The aerogel precursor sol according to any of claims 1 to 11, further comprising a second solvent which is different from the first solvent.

14. The aerogel precursor sol according to claim 13, wherein said second solvent is an alcohol.

15. The aerogel precursor sol according to claim 13, wherein said second solvent is ethanol.

16. The aerogel precursor sol according to any of claims 1 to 15, further comprising a pH modification

agent.

17. The aerogel precursor sol according to any of claims 1 to 15, further comprising an acid.

18. The aerogel precursor sol according to claim 17, wherein said acid is nitric acid.

19. The aerogel precursor sol according to any of claims 1 to 15, wherein the pH of said sol is between 3 and 5.

20. The aerogel precursor sol according to any of claims 1 to 15, further comprising a gelation catalyst.

21. The aerogel precursor sol according to claim 20, wherein said gelation catalyst is ammonium hydroxide.

22. The aerogel precursor sol according to claim 20, wherein the pH of said sol is between 7 and 9.

23. The aerogel precursor sol according to any of claims 1 to 22, wherein the viscosity of said sol is between 1 and 12 centipoise.

24. The aerogel precursor sol according to any of claims 1 to 15, wherein the viscosity of said sol is between 1 and 5 centipoise.

25. The aerogel precursor sol according to any of claims 1 to 7, wherein said reactant is selected from the group consisting of pyrogenic silica, colloidal silica, and combinations thereof.

26. A non-supercritical method of forming a nanoporous aerogel, said method comprising the steps of:

providing an aerogel precursor sol as defined in any one of claims 1 to 25, said sol being dispersed in said first solvent and a second solvent,

evaporating substantially all of said second solvent while preventing substantial evaporation of said first solvent, and allowing the sol to create a gel, wherein the gel comprises a porous solid and a pore fluid;

continuing to prevent substantial evaporation of said first solvent from said sol until a drying step,

wherein said drying step comprises forming a dry aerogel by removing the pore fluid in a non-supercritical drying atmosphere without substantial collapse of the porous solid;

whereby the skeletal density of the dry aerogel is determined approximately by the volume ratio of said aerogel precursor reactant to said first solvent in said aerogel precursor sol.

27. The method of claim 26, wherein said gel is created before said evaporating step completes.

28. The method of claim 26, wherein said drying step further comprises a solvent exchange.

29. The method of claim 26, further comprising aging said gel before said drying step.

30. The method of claim 29, wherein the aging step is without substantial evaporation of said first solvent.

31. The method of any of claims 26 to 30, wherein said second solvent comprises a reaction product of said gel forming step.

32. The method of any of claims 26 to 31, wherein said second solvent has a vapor pressure which is at least twice the vapor pressure of said first solvent.

33. The method of claim 26, further comprising depositing a thin film of the aerogel precursor sol upon a substrate.

34. The method of claim 33, wherein the substrate is a semiconductor substrate comprising a microelectronic circuit.

35. The method of claim 33 or 34, wherein said depositing a thin film step comprises spin-coating said aerogel precursor sol onto said substrate.

36. The method of any of claims 26 to 35, wherein the first solvent includes glycerol.

37. The method of any of claims 26 to 35, wherein the polyol is a glycol.

38. The method of claim 36, wherein the nanoporous aerogel has a porosity greater than 60% and an average pore diameter less than 20 nm.

39. The method of claim 36, wherein the nanoporous aerogel has a dielectric constant less than 2.0.

40. The method of claim 36, wherein the nanoporous aerogel has a dielectric constant less than 1.8.

41. The method of claim 36, wherein the nanoporous aerogel has a dielectric constant less than 1.4.

42. The method of claim 36, wherein the temperature of the substrate during the drying step is above the freezing temperature of the pore fluid.

43. The method of claim 42, wherein the method does not comprise the step of adding a surface modification agent before the drying step.

44. The method of claim 43, wherein the nanoporous aerogel has a porosity greater than 60% and an average pore diameter less than 20 nm.

45. The method of claim 29, wherein at least part of the aging step is performed in a substantially closed container.

46. The method of claim 29, wherein the temperature of the gel during the aging is greater than 30 degrees C.

47. The method of claim 29, wherein the temperature of the gel during the aging is greater than 80 degrees C.

48. The method of claim 29, wherein the temperature of the gel during the aging is greater than 130 degrees C.

49. The method of claim 36, wherein the porous solid has less than 5% permanent volume reduction

during the pore fluid removal.

50. The method of claim 36, wherein the porous solid has less than 2% permanent volume reduction during the pore fluid removal.

51. The method of claim 36, wherein the porous solid has less than 1% permanent volume reduction during the pore fluid removal.

52. The method of claim 36, wherein the gel creating step is performed in a gelation atmosphere, wherein the concentration of a vapor of the first solvent in the gelation atmosphere is not actively controlled.

53. The method of claim 36, wherein the gel creating step is performed in a gelation atomsphere, wherein the concentration of a vapor of the first solvent in the gelation atmosphere is substantially uncontrolled.

54. The method of claim 36, wherein the reactant is a metal alkoxide selected from the group consisting of tetraethoxysilane, tetramethoxysilane, methlytriethoxysilane, 1,2-Bis(trimethoxysilyl)ethane and combinations thereof.

55. The method of claim 36, wherein the reactant is tetraethoxysilane.

56. The method of claim 36, wherein the dry, porous aerogel has a porosity greater than 60%.

57. The method of claim 56, wherein the porosity is between 60% and 90%.

58. The method of claim 56, wherein the porosity is greater than 80%.

59. The method of claim 36, further comprising the step of replacing at least part of the pore fluid with a liquid before the removing of the pore fluid step.

60. The method of claim 59, wherein the liquid comprises hexanol.

61. The method of claim 36, further comprising the step of annealing the dry, porous aerogel.

62. The method of claim 36, wherein the pressure of the drying atmosphere is less than 3 MPa.

Claims:

1. Metallhaltiges Vorlaufersol fur ein Aerogel mit einem Aerogelvorlaufer-Reaktant, der aus der aus Metallalkoxiden, wenigstens teilweise hydrolysierten Metallalkoxiden, dispersen Metalloxiden und Kombinationen derselben bestehenden Gruppe ausgewahlt ist, und mit einem Polyol als einem ersten Losungsmittel, wobei das Polyol aus der aus Glycerol, Ethylenglycol, 1,4-Butylenglycol, 1,5-Pentandiol, 1,2,4-Butantriol, 1,2,3-Butantriol, 2-Methylpropantriol, 2-(Hydroxymethyl)-1,3-propandiol, 1-4,1-4-Butandiol, 2-Methyl-1,3-propandiol und Kombinationen derselben bestehenden Gruppe ausgewahlt ist, wobei das Molverhaltnis der Molekule des ersten Losungsmittels zu den Metallatomen in dem Reaktant mindestens 1:16 betragt.

2. Vorlaufersol fur ein Aerogel nach Anspruch 1, bei dem das Polyol Glycerol ist.

3. Vorlaufersol fur ein Aerogel nach Anspruch 1, bei dem das erste Losungsmittel Ethylenglycol ist.

4. Vorlaufersol fur ein Aerogel nach einem der Anspruche 1 bis 3, bei dem das Molverhaltnis der Molekule des ersten Losungsmittels zu den Metallatomen in dem Reaktant nicht groser ist als 12:1.

5. Vorlaufersol fur ein Aerogel nach einem der Anspruche 1 bis 3, bei dem das Molverhaltnis der Molekule des ersten Losungsmittels zu den Metallatomen in dem Reaktant zwischen 1:2 und 12:1 liegt.

6. Vorlaufersol fur ein Aerogel nach einem der Anspruche 1 bis 3, bei dem das Molverhaltnis der Molekule des ersten Losungsmittels zu den Metallatomen in dem Reaktant zwischen 1:4 und 4:1 liegt.

7. Vorlaufersol fur ein Aerogel nach einem der Anspruche 1 bis 3, bei dem das Molverhaltnis der Molekule des ersten Losungsmittels zu den Metallatomen in dem Reaktant zwischen 2,5:1 und 12:1 liegt.

8. Vorlaufersol fur ein Aerogel nach einem der Anspruche 1 bis 7, bei dem der Reaktant ein Metallalkoxid ist, das aus der aus Tetraethoxysilan, Tetramethoxysilan, Methyltriethoxysilan, 1,2-Bis (trimethoxysilyl)ethan und Kombinationen derselben bestehenden Gruppe ausgewahlt ist.

9. Vorlaufersol fur ein Aerogel nach einem der Anspruche 1 bis 7, bei dem der Reaktant Tetraethoxysilan ist.

10. Vorlaufersol fur ein Aerogel nach Anspruch 9, bei dem das Tetraethoxysilan wenigstens teilweise hydrolysiert ist.

11. Vorlaufersol fur ein Aerogel nach einem der Anspruche 1 bis 7, bei dem das Metall in dem Aerogelvorlaufers-Reaktant Silicium ist.

12. Vorlaufersol fur ein Aerogel nach einem der Anspruche 1 bis 11, das ferner Wasser umfast.

13. Vorlaufersol fur ein Aerogel nach einem der Anspruche 1 bis 11, das ferner ein zweites, von dem ersten Losungsmittel verschiedenes Losungsmittel umfast.

14. Vorlaufersol fur ein Aerogel nach Anspruch 13, bei dem das zweite Losungsmittel ein Alkohol ist.

15. Vorlaufersol fur ein Aerogel nach Anspruch 13, bei dem das zweite Losungsmittel Ethanol ist.

16. Vorlaufersol fur ein Aerogel nach einem der Anspruche 1 bis 15, das ferner ein den pH-Wert modifizierendes Mittel umfast.

17. Vorlaufersol fur ein Aerogel nach einem der Anspruche 1 bis 15, das ferner eine Saure umfast.

18. Vorlaufersol fur ein Aerogel nach Anspruch 17, bei dem die Saure Salpetersaure ist.

19. Vorlaufersol fur ein Aerogel nach einem der Anspruche 1 bis 15, bei dem der pH-Wert des Sols zwischen 3 und 5 liegt.

20. Vorlaufersol fur ein Aerogel nach einem der Anspruche 1 bis 15, das ferner einen Gelierkatalysator umfast.

21. Vorlaufersol fur ein Aerogel nach Anspruch 20, bei dem der Gelierkatalysator Ammoniumhydroxid ist.

22. Vorlaufersol fur ein Aerogel nach Anspruch 20, bei dem der pH-Wert des Sols zwischen 7 und 9 liegt.

23. Vorlaufersol fur ein Aerogel nach einem der Anspruche 1 bis 22, bei dem die Viskositat des Sols zwischen 1 und 12 Centipoise betragt.

24. Vorlaufersol fur ein Aerogel nach einem der Anspruche 1 bis 15, bei dem die Viskositat des Sols zwischen 1 und 5 Centipoise betragt.

25. Vorlaufersol fur ein Aerogel nach einem der Anspruche 1 bis 7, bei dem der Reaktant aus der aus pyrogenem Siliciumdioxid, kolloidalem Siliciumdioxid und Kombinationen derselben bestehenden Gruppe ausgewahlt ist.

26. Nichtsuperkritisches Verfahren zur Bildung eines nanoporosen Aerogels, wobei das Verfahren die folgenden Schritte umfast:

Bereitstellen eines Vorlaufersols fur ein Aerogel nach einem der Anspruche 1 bis 25, wobei das Sol in dem ersten Losungsmittel und in einem zweiten Losungsmittel dispergiert ist,

Verdampfen im wesentlichen des gesamten zweiten Losungsmittels, wahrend das Verdampfen des ersten Losungsmittels weitgehend verhindert wird, und Erzeugung eines Gels aus dem Sol, wobei das Gel einen porosen Feststoff und ein Porenfluid umfast;

weiterhin weitgehendes Verhindern des Verdampfens des ersten Losungsmittels aus dem Sol bis zu einem Trocknungsschritt,

wobei wahrend des Trocknens ein trockenes Aerogel gebildet wird, indem das Porenfluid in einer nichtsuperkritischen Trocknungsatmosphare entfernt wird, ohne das der porose Feststoff im wesentlichen zusammenfallt;

wodurch die Gerustdichte des trockenen Aerogels ungefahr durch das Volumenverhaltnis des Aerogelvorlaufer-Reaktanten zu dem ersten Losungsmittel in dem Vorlaufersol fur das Aerogel bestimmt wird.

27. Verfahren nach Anspruch 26, bei dem das Gel vor dem Ende des Verdampfungsschrittes entsteht.

28. Verfahren nach Anspruch 26, bei dem der Schritt des Trocknens ferner einen Losungsmittelaustausch umfast.

29. Verfahren nach Anspruch 26, bei dem ferner das Gel vor dem Trocknen gealtert wird.

30. Verfahren nach Anspruch 29, bei dem das Altern im wesentlichen ohne Verdampfen des ersten Losungsmittels durchgefuhrt wird.

31. Verfahren nach einem der Anspruche 26 bis 30, bei dem das zweite Losungsmittel ein Reaktionsprodukt aus dem Schritt der Gelbildung umfast.

32. Verfahren nach einem der Anspruche 26 bis 31, bei dem das zweite Losungsmittel einen Dampfdruck hat, der mindestens zweimal so hoch ist wie der Dampfdruck des ersten Losungsmittels.

33. Verfahren nach Anspruch 26, bei dem ferner eine dunne Schicht des Vorlaufersols fur ein Aerogel auf ein Substrat aufgebracht wird.

34. Verfahren nach Anspruch 33, bei dem das Substrat ein Halbleitersubstrat mit einem mikroelektronischen Schaltkreis ist.

35. Verfahren nach Anspruch 33 oder 34, bei dem das Aufbringen einer Dunnschicht das Aufschleudern des Vorlaufersols fur ein Aerogel auf das Substrat umfast.

36. Verfahren nach einem der Anspruche 26 bis 35, bei dem das erste Losungsmittel Glycerol umfast.

37. Verfahren nach einem der Anspruche 26 bis 35, bei dem das Polyol ein Glycol ist.

38. Verfahren nach Anspruch 36, bei dem das nanoporose Aerogel eine Porositat von mehr als 60 % und einen durchschnittlichen Porendurchmesser von weniger als 20 nm hat.

39. Verfahren nach Anspruch 36, bei dem das nanoporose Aerogel eine Dielektrizitatskonstante von weniger als 2,0 hat.

40. Verfahren nach Anspruch 36, bei dem das nanoporose Aerogel eine Dielektrizitatskonstante von weniger als 1,8 hat.

41. Verfahren nach Anspruch 36, bei dem das nanoporose Aerogel eine Dielektrizitatskonstante von weniger als 1,4 hat.

42. Verfahren nach Anspruch 36, bei dem die Temperatur des Substrats wahrend des Trocknens uber der Gefriertemperatur des Porenfluids liegt.

43. Verfahren nach Anspruch 42, bei dem im Verlauf des Verfahrens kein die Oberflache modifizierendes Mittel vor dem Trocknen zugesetzt wird.

44. Verfahren nach Anspruch 43, bei dem das nanoporose Aerogel eine Porositat von mehr als 60 % und einen durchschnittlichen Porendurchmesser von weniger als 20 nm hat.

45. Verfahren nach Anspruch 29, bei dem wenigstens ein Teil des Alterns in einem im wesentlichen geschlossenen Behalter durchgefuhrt wird.

46. Verfahren nach Anspruch 29, bei dem die Temperatur des Gels wahrend des Alterns groser ist als 30 (degree)C.

47. Verfahren nach Anspruch 29, bei dem die Temperatur des Gels wahrend des Alterns groser ist als 80 (degree)C.

48. Verfahren nach Anspruch 29, bei dem die Temperatur des Gels wahrend des Alterns groser ist als 130(degree)C.

49. Verfahren nach Anspruch 36, bei dem der porose Feststoff wahrend des Entfernens des Porenfluids

weniger als 5 % bleibende Volumenverminderung erfahrt.

50. Verfahren nach Anspruch 36, bei dem der porose Feststoff wahrend des Entfernens des Porenfluids weniger als 2 % bleibende Volumenverminderung erfahrt.

51. Verfahren nach Anspruch 36, bei dem der porose Feststoff wahrend des Entfernens des Porenfluids weniger als 1 % bleibende Volumenverminderung erfahrt.

52. Verfahren nach Anspruch 36, bei dem der Schritt der Gelbildung in einer Gelieratmosphare durchgefuhrt wird, wobei die Dampfkonzentration eines Dampfes des ersten Losungsmittels in der Gelieratmosphare nicht aktiv gesteuert wird.

53. Verfahren nach Anspruch 36, bei dem der Schritt der Gelbildung in einer Gelieratmosphare durchgefuhrt wird, wobei die Dampfkonzentration eines Dampfes des ersten Losungsmittels in der Gelieratmosphare im wesentlichen ungesteuert ist.

54. Verfahren nach Anspruch 36, bei dem der Reaktant ein Metallalkoxid ist, das aus der aus Tetraethoxysilan, Tetramethoxysilan, Methyltriethoxysilan, 1,2-Bis(trimethoxysilyl)ethan und Kombinationen derselben bestehenden Gruppe ausgewahlt ist.

55. Verfahren nach Anspruch 36, bei dem der Reaktant Tetraethoxysilan ist.

56. Verfahren nach Anspruch 36, bei dem das trockene, porose Aerogel eine Porositat von mehr als 60 % aufweist.

57. Verfahren nach Anspruch 56, bei dem die Porositat zwischen 60 % und 90 % liegt.

58. Verfahren nach Anspruch 56, bei dem die Porositat mehr als 80 % betragt.

59. Verfahren nach Anspruch 36, bei dem ferner wenigstens ein Teil des Porenfluids durch eine Flussigkeit ersetzt wird, bevor das Porenfluid entfernt wird.

60. Verfahren nach Anspruch 59, bei dem die Flussigkeit Hexanol umfast.

61. Verfahren nach Anspruch 36, bei ferner das trockene, porose Aerogel ausgeheizt wird.

62. Verfahren nach Anspruch 36, bei dem der Druck der Trocknungsatmosphare weniger als 3 MPa betragt.

Claims:

1. Sol de precurseur d'aerogel a base de metal, comprenant un reactif precurseur d'aerogel choisi parmi les alcoolates de metal, les alcoolates de metal au moins partiellement hydrolyses, les oxydes de metal particulaires et leurs associations, et un polyol en tant que premier solvant, le polyol etant choisi parmi le glycerol, l'ethylene glycol, le 1,4-butylene glycol, le 1,5-pentanediol, le 1,2,4-butanetriol, le 1,2,3-butanetriol, le 2-methyl-propanetriol, le 2-(hydroxymethyl)-1,3-propanediol, le 1-4,1-4-butanediol, le 2-methyl-1,3-propanediol et leurs associations, le rapport molaire desdites molecules de premier solvant aux atomes de metal dans ledit reactif etant d'au moins 1:16.

2. Sol de precurseur d'aerogel selon la revendication 1, dans lequel ledit polyol est le glycerol.

3. Sol de precurseur d'aerogel selon la revendication 1, dans lequel ledit premier solvant est l'ethylene glycol.

4. Sol de precurseur d'aerogel selon l'une quelconque des revendications 1 a 3, dans lequel le rapport molaire desdites molecules de premier solvant aux atomes de metal dans ledit reactif, n'est pas superieur a 12:1.

5. Sol de precurseur d'aerogel selon l'une quelconque des revendications 1 a 3, dans lequel le rapport molaire desdites molecules de premier solvant aux atomes de metal dans ledit reactif, est de 1 : 2 a 12:1.

6. Sol de precurseur d'aerogel selon l'une quelconque des revendications 1 a 3, dans lequel le rapport molaire desdites molecules de premier solvant aux atomes de metal dans ledit reactif, est de 1:4 a 4:1.

7. Sol de precurseur d'aerogel selon l'une quelconque des revendications 1 a 3, dans lequel le rapport molaire desdites molecules de premier solvant aux atomes de metal dans ledit reactif, est de 2,5:1 a 12:1.

8. Sol de precurseur d'aerogel selon l'une quelconque des revendications 1 a 7, dans lequel ledit reactif est un alcoolate de metal choisi parmi le tetraethoxysilane, le tetramethoxysilane, le methyl-triethoxysilane, le 1,2-bis(trimethoxysilyl)ethane et leurs associations.

9. Sol de precurseur d'aerogel selon l'une quelconque des revendications 1 a 7, dans lequel ledit reactif est le tetraethoxysilane.

10. Sol de precurseur d'aerogel selon la revendication 9, dans lequel ledit tetraethoxysilane est au moins partiellement hydrolyse.

11. Sol de precurseur d'aerogel selon l'une quelconque des revendications 1 a 7, dans lequel le metal dans le reactif precurseur d'aerogel est le silicium.

12. Sol de precurseur d'aerogel selon l'une quelconque des revendications 1 a 11, comprenant en outre de l'eau.

13. Sol de precurseur d'aerogel selon l'une quelconque des revendications 1 a 11, comprenant en outre un deuxieme solvant different du premier solvant.

14. Sol de precurseur d'aerogel selon la revendication 13, dans lequel ledit deuxieme solvant est un alcool.

15. Sol de precurseur d'aerogel selon la revendication 13, dans lequel ledit deuxieme solvant est l'ethanol.

16. Sol de precurseur d'aerogel selon l'une quelconque des revendications 1 a 15, comprenant en outre un agent de modification de pH.

17. Sol de precurseur d'aerogel selon l'une quelconque des revendications 1 a 15, comprenant en outre un acide.

18. Sol de precurseur d'aerogel selon la revendication 17, dans lequel ledit acide est l'acide nitrique.

19. Sol de precurseur d'aerogel selon l'une quelconque des revendications 1 a 15, dans lequel le pH dudit

sol est de 3 a 5.

20. Sol de precurseur d'aerogel selon l'une quelconque des revendications 1 a 15, comprenant en outre un catalyseur de gelification.

21. Sol de precurseur d'aerogel selon la revendication 20, dans lequel ledit catalyseur de gelification est l'hydroxyde d'ammonium.

22. Sol de precurseur d'aerogel selon la revendication 20, dans lequel le pH dudit sol est de 7 a 9.

23. Sol de precurseur d'aerogel selon l'une quelconque des revendications 1 a 22, dans lequel la viscosite dudit sol est de 1 a 12 centipoises.

24. Sol de precurseur d'aerogel selon l'une quelconque des revendications 1 a 15, dans lequel la viscosite dudit sol est de 1 a 5 centipoises.

25. Sol de precurseur d'aerogel selon l'une quelconque des revendications 1 a 7, dans lequel ledit reactif est choisi parmi la silice pyrogene, la silice colloidale et leurs associations.

26. Procede non supercritique de formation d'un aerogel nanoporeux, comprenant les etapes consistant :

a former un sol precurseur d'aerogel tel que defini dans l'une quelconque des revendications 1 a 25, ledit sol etant disperse dans ledit premier solvant et un deuxieme solvant,

a evaporer presque la totalite dudit deuxieme solvant en empechant une evaporation importante dudit premier solvant, et a permettre au sol de former un gel, le gel comprenant un solide poreux et un fluide dans les pores ;

a continuer a empecher une evaporation importante dudit premier solvant a partir dudit sol jusqu'a une etape de sechage,

ladite etape de sechage comprenant la formation d'un aerogel sec en eliminant le fluide dans les pores dans une atmosphere de sechage non supercritique sans affaissement important dudit solide poreux ;

grace a quoi la densite du squelette de l'aerogel sec est determinee approximativement par le rapport volumique dudit reactif precurseur d'aerogel audit premier solvant dans ledit sol precurseur d'aerogel.

27. Procede selon la revendication 26, dans lequel ledit gel est forme avant achevement de ladite etape d'evaporation.

28. Procede selon la revendication 26, dans lequel ladite etape de sechage comprend en outre un echange de solvant.

29. Procede selon la revendication 26, comprenant en outre un vieillissement dudit gel avant ladite etape de sechage.

30. Procede selon la revendication 29, dans lequel ladite etape de sechage est effectuee sans evaporation importante dudit premier solvant.

31. Procede selon l'une quelconque des revendications 26 a 30, dans lequel ledit deuxieme solvant

comprend le produit de reaction de ladite etape de formation de gel.

32. Procede selon l'une quelconque des revendications 26 a 31, dans lequel ledit deuxieme solvant a une pression de vapeur qui est au moins le double de la pression vapeur dudit premier solvant.

33. Procede selon la revendication 26, comprenant en outre un depot d'un film mince du sol de precurseur d'aerogel sur un substrat.

34. Procede selon la revendication 33, dans lequel le substrat est un substrat semi-conducteur comprenant un circuit micro-electronique.

35. Procede selon la revendication 33 ou 34, dans lequel ladite etape de depot de film mince comprend un depot par centrifugation dudit sol de precurseur d'aerogel sur ledit substrat.

36. Procede selon l'une quelconque des revendications 26 a 35, dans lequel le premier solvant comprend du glycerol.

37. Procede selon l'une quelconque des revendications 26 a 35, dans lequel le polyol est un glycol.

38. Procede selon la revendication 36, dans lequel l'aerogel nanoporeux a une porosite superieure a 60 % et un diametre de pore moyen inferieur a 20 nm.

39. Procede selon la revendication 36, dans lequel l'aerogel nanoporeux a une constante dielectrique inferieure a 2,0.

40. Procede selon la revendication 36, dans lequel l'aerogel nanoporeux a une constante dielectrique inferieure a 1,8.

41. Procede selon la revendication 36, dans lequel l'aerogel nanoporeux a une constante dielectrique inferieure a 1,4.

42.Procede selon la revendication 36, dans lequel la temperature du substrat au cours de l'etape de sechage est superieure a la temperature de congelation du fluide dans les pores.

43. Procede selon la revendication 42, ne comprenant pas l'etape d'addition d'un agent de modification de surface avant l'etape de sechage.

44. Procede selon la revendication 43, dans lequel l'aerogel nanoporeux a une porosite superieure a 60 % et un diametre de pore moyen inferieur a 20 nm.

45. Procede selon la revendication 29, dans lequel au moins une partie de l'etape de vieillissement est effectuee dans un recipient pratiquement ferme.

46. Procede selon la revendication 29, dans lequel la temperature du gel au cours du vieillissement est superieure a 30 (degree)C.

47. Procede selon la revendication 29, dans lequel la temperature du gel au cours du vieillissement est superieure a 80 (degree)C.

48. Procede selon la revendication 29, dans lequel la temperature du gel au cours du vieillissement est

superieure a 130 (degree)C.

49. Procede selon la revendication 36, dans lequel le solide poreux a un taux de reduction de volume permanent inferieur a 5 % au cours du retrait du fluide des pores.

50. Procede selon la revendication 36, dans lequel le solide poreux a un taux de reduction de volume permanent inferieur a 2 % au cours du retrait du fluide des pores.

51. Procede selon la revendication 36, dans lequel le solide poreux a un taux de reduction de volume permanent inferieur a 1 % au cours du retrait du fluide des pores.

52. Procede selon la revendication 36, dans lequel l'etape de formation de gel est effectuee dans une atmosphere de gelification dans laquelle la concentration de la vapeur du premier solvant dans l'atmosphere de gelification n'est pas activement ajustee.

53. Procede selon la revendication 36, dans lequel l'etape de formation de gel est effectuee dans une atmosphere de gelification, la concentration de la vapeur du premier solvant dans l'atmosphere de gelification etant a peu pres non ajustee.

54. Procede selon la revendication 36, dans lequel le reactif est un alcoolate de metal choisi parmi le tetraethoxysilane, le tetramethoxysilane, le methyltriethoxysilane, le 1,2-bis(trimethoxysilyl)-ethane et leurs associations.

55. Procede selon la revendication 36, dans lequel le reactif est le tetraethoxysilane.

56. Procede selon la revendication 36, dans lequel l'aerogel poreux et sec, a une porosite superieure a 60 %.

57. Procede selon la revendication 56, dans lequel la porosite est de 60 % a 90 %.

58. Procede selon la revendication 56, dans lequel la porosite est superieure a 80 %.

59. Procede selon la revendication 36, comprenant en outre l'etape de remplacement d'au moins une partie du fluide dans les pores par un liquide avant l'etape de retrait du fluide des pores.

60. Procede selon la revendication 59, dans lequel le liquide comprend de l'hexanol.

61. Procede selon la revendication 36, comprenant en outre l'etape de recuit de l'aerogel poreux et sec.

62. Procede selon la revendication 36, dans lequel la pression de l'atmosphere de sechage est inferieure a 3 MPa.

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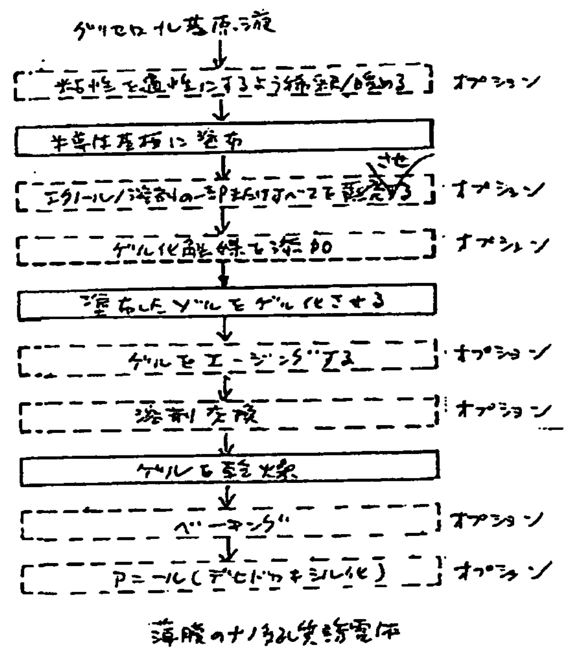
最終頁に続く

(54)【発明の名称】　ナノ多孔質アエロゲル用の低揮発性溶剤基前駆物質

(57)【要約】

【課題】雰囲気制御を行うことなく多孔率が制御された薄膜のナノ多孔質エーロゲルをデポジットし、ゲル化し、エージングし、乾燥すること。

【解決手段】アエロゲル前駆物質ゾルは、金属基アエロゲル前駆物質反応体と、ポリオールを含む第1溶剤とを備え、反応体における金属原子に対する第1溶剤の分子のモル比が少なくとも1：16となっている。好ましくは第1溶剤はグリセロールであり、好ましくはこのアエロゲル前駆物質反応体は、金属アルコキシド、少なくとも一部が加水分解された金属アルコキシド、粒状金属酸化物およびそれらの組み合わせから成る群から選択できる。一般に反応体における金属原子に対する第1溶剤の分子のモル比は12：1以下であり、好ましくは反応体における金属原子に対する第1溶剤の分子のモル比は1：2～12：1の間である。



【特許請求の範囲】

【請求項1】 アエロゲル前駆物質反応体と、ポリオールを含む第1溶剤とを備え、前記反応体における金属原子に対する前記第1溶剤の分子のモル比が少なくとも1：16である金属基ナノ多孔質アエロゲル前駆物質ゾル。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、一般的にはナノ多孔質（孔径がナノメータの大きさの微細多孔質）アエロゲルを製造するための前駆物質に関し、より詳細にはバルクおよび薄膜アエロゲルの準臨界的および過臨界的乾燥に適した前駆物質に関する。

【0002】

【従来技術】アエロゲルは多孔質のシリカ材料であり、膜（例えば半導体デバイス上に設けられる電気絶縁体または光学的コーティング）またはバルク（例えば熱絶縁体）のような種々の用途に対し使用できる。説明を簡単にするため、本明細書における実施例は半導体デバイス上に設けられる電気絶縁体として主に使用するものとする。

【0003】半導体はコンピュータおよびテレビのような電子デバイス用の集積回路で広く使用されている。半導体および電子機器メーカーのみならずエンドユーザーも、消費電力が少ないが、より小さいパッケージでより短い時間で作動できる集積回路を望んでいる。しかしながら、これら要望の多くは互いに矛盾するものである。例えば、所定の回路で大きさを0．5ミクロン〜0．25ミクロンへ縮小するだけでエネルギー消費量および熱の発生が30％だけ増加し得る。また、寸法を小さくする結果、一般にチップ間で信号を送る導線の間の容量結合すなわちクロストークが増えることとなる。このような効果は達成できる速度を制限するだけでなく、デバイスの適正な作動を保証するのに使用されるノイズマージンを劣化する。エネルギーの使用量／熱発生量およびクロストーク効果を減少する1つの方法は、導線を分離する絶縁体、すなわち誘電体の誘電率を増すことである。ルナード外に発行された米国特許第5，470，802号は、これら解決方法のうちのいくつかに対する背景技術を提供するものである。

【0004】ある種の材料、すなわちナノ多孔質誘電体には半導体製造のための最も将来性のある新材料のうちのいくつかが含まれる。これら誘電体材料は、例えばシリカのような固体構造を含み、この固体構造は一般に数ナノメータの大きさの直径を有する孔の相互に絡み合ったネットワークが通っている。これら材料には極めて大きな多孔率を形成でき、これに対応して誘電率は一般に密なシリカの誘電率の半分よりも小さくなる。しかしながら、大きな多孔率にも拘わらず強度が大きく、現在のほとんどの半導体製造プロセスとのコンパーチビリティに優れたナノ多孔質の誘電体を製造できることが判っている。従って、ナノ多孔質の誘電体は一般的な半導体誘電体、例えば密なシリカに対する可能性のある低誘電率の置換物となる。

【0005】ナノ多孔質の誘電体を形成するための好ましい方法は、ゾルーゲル技術を使用する方法である。ここで、「ゾルーゲル」なる用語は製品を記述する用語ではなく、液体内の固体粒子のコロイド状サスペンションであるゾルが固体粒子の成長および相互結合によりゲルに変化する反応機構を意味する用語である。ゾル内で反応が継続することによりゾル内の1つ以上の分子が最終的に巨視的な大きさに達し、ほぼゾル内全体にわたって延びる固体ネットワークを形成し得るという1つの理論がある。この点で（ゲル点と称される）において、この物質はゲルと称されている。このような定義によれば、ゲルとは連続的な液相を囲む連続的な固体骨格を含む物質のことである。骨格が多孔質であれば、本明細書で使用する用語「ゲル」とは孔内の流体を囲む連続多孔固体構造を意味する。

【0006】ゾルを形成する1つの方法には、加水分解と縮合反応を利用する方法があり、これら反応により溶液内の多官能価モノマーが重合し、比較的大きな分岐の多い粒子となり得る。かかる重合に適した多くのモノマーとして金属アルコキシがある。例えばテトラエトキシシラン（TEOS）モノマーは次の反応により水中で一部が加水分解し得る。

【0007】

【化1】$Si(OEt)_4 + H_2O \rightarrow HO-Si(OEt)_3 + EtOH$

【0008】反応条件は各モノマーがこれを部分的または完全に加水分解するような所望の回数の加水分解反応を平均として行うように制御できる。完全に加水分解されたTEOSは$Si(OH)_4$となる。分子が少なくとも部分的に加水分解されると、2つの分子は次のような縮合反応で共に結合し得る。

【0009】

【化2】$(OEt)_3Si-OH + HO-Si(OH)_3 \rightarrow (OEt)_3Si-O-Si(OH)_3 + H_2O$

または

$(OEt)_3Si-OEt + HO-Si(OEt)_3 \rightarrow (OEt)_3Si-O-Si(OEt)_3 + EtOH$

【0010】よって、2つの分子の結合によりオリゴマーが形成され、水またはエタノール分子を遊離する。これら反応によって形成されたオリゴマー内のSi−O−Si結合は、各端部に更に加水分解および縮合するのに利用できる3つの部位を有する。従って、文字どおり数千個のモノマーから1つの分岐の多いポリマー分子を形成するよう、この分子に多少ランダム状に付加的モノマーすなわちオリゴマーを付加することができる。本明細書に記載したオリゴマー化された金属アルコキシは、少

なくとも２つのアルコキシモノマーから形成された分子を含むが、ゲルを含んでいない。

【００１１】ゾルーゲル反応はキセロゲルおよびアエロゲル膜堆積（デポジション）のための基礎となる。代表的な薄膜キセロゲルプロセスではゲル化していない前駆物質のゾルを（例えばスプレーコーティング、浸漬コーティングまたはスピニングコーティングにより）基板に塗布し、厚さが数ミクロン以下の大きさの薄膜を形成し、これをゲル化し、乾燥して密な膜を形成できる。前駆物質のゾルは原液と溶剤を含むことが多く、ゲル化を速くするために前駆物質のゾルのｐＨを変えるゲル化触媒を含むこともある。コーティング中およびコーティング後はゾルの薄膜内の揮発性成分は通常急速に蒸発する。従って、膜が急速に崩壊して密な膜となる際にデポジション、ゲル化および乾燥段階が（少なくともある程度）同時に生じ得る。これと対照的にアエロゲルプロセスは湿潤ゲルの乾燥中に主に孔の崩壊を防止することにより、キセロゲルプロセスと異なっている。孔の崩壊を防止するいくつかの方法として（上記米国特許第５，４７０，８０２号に記載されているような）縮合禁止改質剤により湿潤ゲルを処理する方法と、過臨界的に孔内の流体を抽出する方法がある。

【００１２】アエロゲルとキセロゲルとでは半導体薄膜のナノ多孔質誘電体用には２つの乾燥ゲル材料として好ましい。代表的な薄膜キセロゲル方法は限定された多孔率（大きな孔径で６０％までであるが、一般にはサブミクロンの半導体製造で有効な孔径ではほぼ５０％よりも低い）を有する膜を製造する。従来のキセロゲルのいくつかは５０％よりも大きい多孔率を有するが、これら従来のキセロゲルはほぼ大きな孔径（一般に１００ｎｍ以上）を有していた。これら大きな孔径のゲルは機械的強度がかなり小さい。更にこのような大きな孔径により、ゲルはマイクロ回路上の小さい（一般に１マイクロメータよりも小さく、潜在的には１００ｎｍよりも小さい）パターン形成されたギャップを充填するのに不適当となり、それらの光学的膜の用途をそれよりも長い波長だけに限定されている。他方、ナノ多孔質のアエロゲル薄膜は極めて微細な孔径と関連したほとんど望ましい多孔率をに形成できる。一般に、ここで使用されるナノ多孔質材料は約２５ｎｍよりも小さく、好ましくは２０ｎｍより小さい（より好ましくは１０ナノメートル、更により好ましくは5ナノメートルよりも小）平均孔径を有する。この方法を使用する多くの配合では半導体用の代表的なナノ多孔質材料は全体に少なくとも１ｎｍの平均孔径を有し得るが、少なくとも３ｎｍの平均孔径を有することのほうが多い。ナノ多孔質無機誘電体はナノ多孔質金属酸化物、特にナノ多孔質シリカを有する。

【００１３】

【発明が解決使用とする課題】多くのナノ多孔質薄膜用用途では光学的膜として、またはマイクロ電子技術で使用されるアエロゲルおよびキセロゲルでは、膜厚およびアエロゲルの密度を正確に制御することが好ましい。機械的強度、孔径および誘電率を含む膜のいくつかの重要な性質は、アエロゲルの密度に関連している。現在ではアエロゲルの密度および膜厚はゾルを基板に塗布した時のゾルの粘性に関連していることが判っている。このことは、これまで認識されていない問題を提起している。この問題とは、従来の前駆物質のゾルおよびデポジション方法を用いると、アエロゲルの密度と膜厚の双方を独立して、かつ正確に制御することが極めて困難であるということである。

【００１４】ナノ多孔質誘電薄膜はパターン化されたウェーハにデポジットでき、パターン化された導線レベルにデポジットされることが多い。現在ではかかる導線間のギャップが正しく充填され続け、ゲルの表面がほぼプレーナー（平面）状に留まるように保証するため、ゲル化が開始する前にゾルのデポジションを完了しなければならないことが判っている。この目的のために、ゲル化後、例えばエージング中に孔内の流体が大幅に蒸発しないことも好ましい。不幸なことに、プロセスを簡略化するためにデポジション後はできるだけ速やかにゲル点に到達できることも好ましく、薄膜のゲル化をスピードアップする１つの方法は蒸発するように放置することである。アエロゲルデポジション用に適した前駆体ゾルは膜厚、アエロゲル密度、ギャップの充填および平面度を制御でき、デポジション前に比較的安定であり、デポジション後も比較的速やかにゲル化し、かなりの蒸発をすることなくエージングするものでなければならないと認識されている。

【００１５】多溶剤前駆物質ゾルからエージング薄膜を制御しながらデポジットできる方法が現在では見いだされている。この方法ではゾルの粘性と膜厚とを比較的別々に制御できる。これにより膜厚は第１の既知の値から溶剤の比率およびスピン条件によて設定可能な第２の既知の値へ短時間で変更可能となるので、膜厚をアエロゲル密度と独立して維持し、高速ゲル化が可能となる。しかしながら同時に、スピン条件および膜厚と別個にデポジション前に前駆物質ゾル内で乾燥時の膜内の固体と液体の比率（従ってアエロゲルの密度）を正確に決定できる。

【００１６】デポジションの問題と粘性制御および密度制御の副次的問題とをこのように新しく分けたとしても、我々の経験ではキセロゲルおよびアエロゲルを形成するための薄膜ゾルーゲル技術では一般に、乾燥前、例えばゲル化後およびエージング中の蒸発を制限するよう、ある方法、例えば雰囲気制御が一般に必要であることが判っている。原則的にはこの蒸発速度制御はウェーハ上の溶剤蒸気密度を制御することによって達成できる。しかしながら我々の経験では溶剤の蒸発レートは蒸気濃度および温度のわずかな変化に極めて影響されるこ

とが判っている。このプロセスを有効に理解できるようにするため、我々はウェーハからのいくつかの溶剤の等温蒸発を%濃度の関数としてモデル化した。これら溶剤のいくつかに対する周辺温度での蒸発レートが図1に示されている。この蒸発をプロセス時の問題としないようにするためには、蒸発レートと処理時間（好ましくは数分の大きさ）の積を膜厚よりも大幅に小さくしなければならない。このことは、エタノールのような溶剤に対してはウェーハ上の雰囲気を９０％を越える飽和度に維持しなければならないことを示唆している。しかしながら雰囲気が飽和状態または過飽和状態に達することができるようにすることに関連する問題が生じ得る。この問題のいくつかは薄膜上の雰囲気の成分の凝縮と関連している。ゲル化した薄膜またはゲル化していない薄膜上での凝縮は十分にエージングされていない膜内に欠陥を生じさせることが判っている。従って、一般に成分を飽和させないように雰囲気を制御することが好ましい。

【００１７】

【課題を解決するための手段】我々は高揮発性の溶剤を使用することなく、かつ溶剤の雰囲気を正確に制御することなく、雰囲気をあまり制御しないで低揮発性溶剤を使用することがより良好な解決案であることを発見した。この前提条件を検討したところ、グリセロールが優れた溶剤となることを発見した。

【００１８】グリセロールを使用することによりデポジット中、ゲル化中および／またはエージング中の必要な雰囲気制御を（従来の溶剤と比較して）ゆるやかにできる。この理由は、まだ飽和を回避することは好ましいが、過度の蒸発をすることなく雰囲気溶剤の濃度を低かできるからである。図２は、温度および雰囲気溶剤の濃度と共にグリセロールの蒸発レートがどのように変化するかを示している。我々の経験によれば、グリセロールを用いると雰囲気を全く制御することなく、またはほぼ制御することなく、デポジット、ゲル化およびエージングにより許可できるゲルを形成できることが判った。

【００１９】ナノ多孔質の誘電体を製造する際には湿潤ゲル薄膜にエージングとして知られているプロセスを施すことが好ましい。加水分解および縮合反応はゲル点で停止せず、反応が目的を果たして停止するまでゲルを再構成し、エージングし続ける。エージング中、固体構造部分の優先的な溶解および再デポジションにより強度が増し、孔径がより均一となり、乾燥中の孔の耐崩壊性が増すことを含む有利な結果が得られると考えられる。不幸なことにバルクゲルに使用される従来のエージング技術は半導体プロセスにおける薄膜のエージングにはあまり適しておらず、この理由の一部はこのエージング技術は一般に基板を液体に浸漬することを必要とし、かつ一部の理由として完了までに数日または数週間もかかるということも認識している。本発明の１つの特徴として、湿潤ゲル薄膜を液体に浸漬したり、早期に乾燥したりすることを行わず、かつ驚くことにかかる薄膜を数分でエージングできる気相エージング技術が挙げられる。

【００２０】また、アエロゲルは膜またはバルク状態を含む種々の用途に対して使用できるナノ多孔質材料である。しかしながら、膜製造プロセスで生じる問題はバルクプロセス時の問題と異なっているので、実際には膜処理はバルク処理に類似していないと認識すべきである。

【００２１】一般に、飽和状態の雰囲気内でのエージングは液体浸漬エージングに関連した問題を防止することを発見した。更に本発明のこの特徴によれば、高温で湿潤ゲルをエージングするためのいくつかの解決方法が提供される。この方法は湿潤ゲルが孔内の低沸点液を元々含んでいる場合でも使用できる。しかしながらこれら方法は、低揮発性溶剤を用いる場合に、より良好に働く。最後に、本発明のこの特徴によれば、エージングをスピードアップするため、エージング雰囲気にオプションの気相エージング触媒を添加することが考慮される。

【００２２】薄膜はエージングが生じるため、所定期間の間、極めて一定に保持すべき極めて少量の孔内流体を含むので薄膜形成時に湿潤ゲルをエージングすることは困難である。エージングによってネットワークを強化する前に膜から孔内流体が蒸発する場合、膜はキセロゲル状に密となる傾向がある。他方、ネットワークが強化される前に雰囲気から薄膜上に過度の孔内流体が凝縮する場合、これによりエージングプロセスが局部的に乱されることがある。

【００２３】従って、エージング中の孔内流体の蒸発レートを制御するある方法は、エージング薄膜製造に有益であると認識している。基本的にはエージング中の蒸発レート制御はウェーハ上の孔内流体蒸気濃度を積極的に制御することによって達成できる。しかしながら１５０ｍｍのウェーハにデポジットされる、例えば１ｍｍの厚さの７０％多孔質湿潤ゲルに含まれる孔内流体の総量はわずか約０．０１２ｍＬであり、この量は流体の１つの３ｍｍ径の液滴に容易に適合する。半導体ウェーハ上のナノ多孔質誘電体に使用される代表的な薄膜は、約１０００分の１の厚みである。従って、エージング中に例えばわずか１％またはそれ以下の孔内流体の蒸発ができるように（雰囲気に溶剤を加えたり、これから除くことにより）孔内流体の蒸気濃度を積極的に制御することにより、困難なことが生じる。すなわち薄膜の表面積が広く、孔内流体のばらつきに対する許容度が極めて小さくなることである。特にこれまで膜製造プロセスが実際上明らかに不可能であった高温での高速エージングをするには、蒸発および凝縮制御が特に重要である。

【００２４】我々はウェーハ上での孔内流体蒸気濃度を積極的に制御することなく、蒸発制御レートの問題を克服した。このような蒸気濃度の代わりに極めて小容積のチャンバー内でウェーハを処理し、湿潤ゲル膜内に含まれる極めて少量の孔内流体を自然に蒸発させることによ

り、処理雰囲気が孔内流体内で実質的に飽和状態となる。実質的に飽和状態の処理雰囲気内で、ある点でウェーハを冷却しないで、この方法は特に高温処理中に一般に避けなければならない凝縮の問題も解決している。

【００２５】本明細書にはアエロゲル前駆物質ゾルが開示されている。このアエロゲル前駆物質ゾルは、金属基アエロゲル前駆物質反応体と、ポリオールを含む第１溶剤とを備え、反応体における金属原子に対する第１溶剤の分子のモル比が少なくとも１：１６となっている。好ましくは第１溶剤はグリセロールであり、好ましくはこのアエロゲル前駆物質反応体は、金属アルコキシド、少なくとも一部が加水分解された金属アルコキシド、粒状金属酸化物およびそれらの組み合わせから成る群から選択できる。一般に反応体における金属原子に対する第１溶剤の分子のモル比は１２：１以下であり、好ましくは反応体における金属原子に対する第１溶剤の分子のモル比は１：２～１２：１の間である。ある実施例では反応体における金属原子に対する第１溶剤の分子のモル比は２．５：１～１２：１の間である。この方法ではナノ多孔質誘電体が６０％以上の多孔率および２５ｎｍよりも小さい平均孔径を有することも好ましい。ある実施例では、アエロゲル前駆物質は第２溶剤も含む。好ましくはこの第２溶剤はグリセロールよりも高い沸点を有する。ある実施例では、第２溶剤はエタノールでよい。ある実施例では、第１溶剤はグリコールも含み、このグリコールはエチレングリコール、１，４ブチレングリコール、１，５ペンタンジオールおよびそれらの組み合わせから成る群から選択されたものである。ある実施例では第１ポリオールは１，２，４－ブタントリオール；１，２，３－ブタントリオール；２－メチルプロパントリオール；および２－（ヒドロキシメチル）－１，３，プロパンジオール；１－４，１－４，ブタンジオール；および２－メチル－１，３－プロパンジオール、およびそれらの組み合わせから成る群から選択されたものである。ある実施例では、この第１ポリオールはエチレングリコール、１，４ブチレングリコール、１，５ペンタンジオールおよびそれらの組み合わせから成る群から選択されたものである。

【００２６】従って、本発明は雰囲気制御を行うことなく、制御された多孔率の薄膜ナノ多孔質アエロゲルをデポジットし、ゲル化し、エージングし、乾燥できるようにするものである。別の特徴によれば、本発明は受動的な雰囲気制御、例えばエージングチャンバーの容積を限定するだけで、制御された多孔率の薄膜ナノ多孔質アエロゲルをデポジットし、ゲル化し、高温で急速エージングし、乾燥できるようにするものである。

【００２７】次の図面を参照すれば、種々の特徴および利点を含む本発明について最良に理解できよう。

【００２８】

【発明の実施の態様】代表的なゾル－ゲル薄膜プロセスは乾燥時に崩壊し、密となるゲルを製造し、よってわずか数％の多孔率しか有しないキセロゲルを形成する。キセロゲル膜形成の制御されない乾燥条件下では、全プロセスが数秒内で完了し得るので、薄膜の形成中にデポジション、凝集、ゲル化および乾燥工程を完全に分離することは困難であるか不可能であった。しかしながら、かかる方法は制御可能な低密度の高多孔率の薄膜をデポジットするには一般に適していないことが判った。この理由は、アエロゲルタイプの乾燥プロセスでは薄膜は乾燥後もほぼ密でない状態に留まり、最終密度は主にゲル化における膜内の固体と液体の比によって決定されるからである。また、特にパターン化されたウェーハを平面状とし、および／またはギャップを充填するのに薄膜が必要な場合、アエロゲル薄膜デポジションには次の基準が好ましいことが判った。

【００２９】１）スピンーオン用途に適した初期粘性

２）デポジション時の安定な粘性

３）ゲル時間における安定な膜厚

４）ゲル時間における所定の固体と液体の比

５）デポジション直後のゲル化

【００３０】これら条件を満たす従来の前駆物質ゾルおよび方法はまだ見いだされていない。しかしながら、本発明によれば、特定の比の少なくとも２つの溶剤で調整されたゾルは、これら条件を満たすように使用できることが判っている。図１５を参照すれば、かかる前駆物質ゾルをデポジットし、ゲル化する方法について最良に理解できよう。

【００３１】図１５に示されるように、時間ｔ＝０では初期膜厚Ｄ０および初期粘性Ｈ０において、ウェーハに多溶剤タイプの前駆物質ゾルをスピニングできる。このスピニングはウェーハからの低揮発性溶剤の蒸発を大幅に抑制する低揮発性溶剤の部分厚を有する制御された雰囲気内で実行することが好ましい。従って、スピンーオン作業の後に低揮発性溶剤を維持し、よって膜厚をＤ１に減少する間の蒸発時間Ｔ１の間にウェーハから高揮発性溶剤を優先的に除く。粘性も、主に好ましくは溶剤の除去により、この時間の間、ｈ１に変化する。理想的にはこの時間の間、ゾル内のプリマークラスターの架橋はほとんど生じないことが好ましい。Ｔ１の終了時にはほとんどすべての高揮発性溶剤を蒸発すべきであり、この時間において、膜厚は安定するか、またはより低いレートで減少し続けるべきであり、よってゲル時間に膜厚の液体と固体の比を所定の値をし、かつ厚みを所定の値とすべきである。

【００３２】時間Ｔ２は蒸発時間Ｔ１の終了点とゲル時間Ｔ１中に生じるゲル点との間を分離させるのが主な目的である。この時間Ｔ２は０よりも長いことが好ましい。しかしながら、ある前駆物質、特により高速のゲル化を促進する溶剤、例えばグリセロールを有する前駆物質は、期間Ｔ１の終了時までにゲル化する。更に時間Ｔ

１またはＴ２の間に制御された雰囲気内に気相状態の触媒、例えばアンモニアを導入してもよい。この触媒は薄膜内に拡散することができ、更にゾルを活性化し、高速の架橋を促進する。Ｔ２の間は蒸発がほとんど生じないか、または全く生じないことが好ましいが、架橋がポリマークラスターをリンクし続けるにつれて粘性は実質的に増加し始めなければならない。

【００３３】ゲル化点後の蒸発の結果、パターン形成されたウェーハに対するギャップ充填および平面度が不良となり得る。従って、ゲル化時間Ｔ３の後に蒸発を制限することによりゲルポイントを通過する前に膜厚をほぼ一定に保持することが好ましい。大きなポリマークラスターが最終的に接合し、薄膜を横断するよう連続的なスパニングクラスターを形成するゲルポイントにゾルが接近するにつれて、時間Ｔ３の間で粘性が著しく変化することが時々ある。

【００３４】この新しい方法の数種の利点は、図１５から明らかである。ゾル粘性および膜厚の双方は急速に変化することが認められるが、一般に同時に変化することは認められない。また、膜厚も第１の既知の値から溶剤比率およびスピン条件によって別々に設定できる第２の公知の値まで変化する。この方法を使用すれば低粘性の膜を塗布し、あらかじめ設定した厚みとなるように迅速に薄くし、所望の密度で容易にゲル化できる。

【００３５】先のパラグラフは乾燥されたゲル密度と別個に前駆物質のゾル粘性を変える方法を挟持している。しかしながら、このパラグラフはどの溶剤が最も適当であるかの問いに答えていない。我々の経験によれば、伝統的なアエロゲル溶剤に対する溶剤蒸発レートは蒸気の濃度および温度のわずかな変化に極めて敏感であることがあることが判っている。このプロセスをより良好に理解するため、我々はウェーハからの等温溶剤蒸発を％飽和度の関数としてモデル化した。このモデル化は物質移動理論に基づくものである。この物質移動理論の良好な文献としてはＲ．Ｂ．バード、Ｗ．Ｅ．スチュワート、Ｅ．Ｎ．ライトフットによる輸送現象（特に第１６章および１７章）がある。これら計算はある範囲の溶剤に対して実行されている。図１にはこれら溶剤のいくつかに対する周辺温度の蒸発レートが示されている。この蒸発をプロセス時の問題としないようにするためには、蒸発レートと処理時間（好ましくは数分の大きさ）の積を膜厚よりも大幅に小さくしなければならない。このことは、エタノールのような溶剤に対してはウェーハ上の雰囲気を９０％を越える飽和度に維持しなければならないことを示唆している。しかしながら雰囲気が飽和状態または超飽和状態に達することができるようにすることに関連する問題が生じ得る。この問題のいくつかは薄膜上の雰囲気の成分の凝縮と関連している。ゲル化した薄膜またはゲル化していない薄膜上での凝縮は十分にエージングされていない膜内に欠陥を生じさせることが判っている。従って、一般に成分を飽和させないように雰囲気を制御することが好ましい。

【００３６】我々は高揮発性の溶剤を使用することなく、かつ溶剤の雰囲気を正確に制御することなく、雰囲気をあまり制御しないで低揮発性溶剤を使用することがより良好な解決案であることを発見した。この前提条件を検討したところ、グリセロールが優れた溶剤となることを発見した。

【００３７】グリセロールを使用することによりデポジット中、ゲル化中および／またはエージング中の必要な雰囲気制御を（従来の溶剤と比較して）ゆるやかにできる。この理由は、まだ飽和を回避することは好ましいが、過度の蒸発をすることなく雰囲気溶剤の濃度を低下できるからである。図２は、温度および雰囲気溶剤の濃度と共にグリセロールの蒸発レートがどのように変化するかを示している。我々の経験によれば、グリセロールを用いると雰囲気を全く制御することなく、またはほぼ制御することなく、デポジット、ゲル化およびエージングにより受け入れ可能なゲルを形成できることが判った。このような最も好ましい方法では、デポジションおよびゲル化中の（実質的に制御されない雰囲気）雰囲気制御は一般にクリーンルームの温度および湿度制御に限定されるが、ウェーハおよび／または前駆物質ゾルは別個の温度制御がされ得る。

【００３８】溶剤としてグリセロールを使用する魅力的な特徴としては、周辺温度で蒸発レートが十分低くされ、よって周辺状態における数時間では薄膜の劇的な収縮を生じないという点が挙げられる。我々の経験ではグリセロールを用いると全く制御しないか、ほぼ制御しない雰囲気内でデポジットし、ゲル化し、エージングすることにより、許容できるゲルを形成できる。グリセロールを用いると、周辺温度での蒸発レートが十分低くなり、よって周辺状態での数時間では薄膜の劇的な収縮が生じない。また、我々の経験によれば、エチレングリコールを用いると全く制御しないか、実質的に制御しない雰囲気内でデポジットし、ゲル化することにより、許容可能なゲルを形成できることも判っている。エチレングリコールを用いると周辺温度での蒸発レートはグリセロールよりも高くなるが、周辺状態での数分では薄膜の劇的な収縮が生じないほど十分低い。しかしながら、エチレングリコール基ゾルは相当するグリセロール基ゾルよりも粘性が大幅に低いので、デポジションが簡単になる。また、グリセロール基ゾル内の孔内流体は相当するエチレングリコール基ゾルよりも表面張力がかなり大きいので、低収縮での乾燥がより困難となる。

【００３９】エチレングリコールおよびグリセロールは低蒸気圧および混和性溶剤として働く他に、ゾルーゲル反応にも関与し得る。このプロセスにおける正確な反応は完全に研究されていないが、ある反応を予想できる。前駆物質としてテトラエトキシシラン（ＴＥＯＳ）を使

用する場合、エチレングリコールはエトキシ基と置換可能である。

【0040】

【化3】$Si(OC_2H_5)_4 + xHOC_2H_4OH \Leftrightarrow Si(OC_2H_5)_{4x}(OC_2H_4OH)_x + xC_2H_5OH$

【0041】同様に、グリセロール溶剤と共に前駆物質としてテトラエトキシシラン（TEOS）を使用する場合、グリセロールはエトキシ基と置換可能である。

【0042】

【化4】

$$Si(OC_2H_5)_4 + x[HOCH_2CH(OH)CH_2OH] \leftrightarrow Si(OC_2H_5)_{4\text{-}x}[OC_3H_5(OH)_2]_x + x[C_2H_5OH]$$

【0043】基本的には、これら化学基の存在および濃度は前駆物質の反応性（例えばゲル時間）を変え、ゲルの微細構造（表面積、孔径分布等）を変え、エージング特性を変えたりゲルの他のほとんどすべての特性を変え得る。

【0044】新しい溶剤系を使用するとゲル時間、粘性、エージング状態および乾燥収縮率を含む広範な処理パラメータが変わり得る。ゲル化時間のようなこれら特性の多くは薄膜上での測定が困難である。バルクの性質と薄膜の性質は異なることがあるが、溶剤系を変えるとどのようにナノ多孔質のシリカプロセスに影響があるかを良好に理解するために、バルクサンプル（例えば30mm長×約5mm径）で一連の実験を行うことが有益であることが多い。

【0045】グリセロールはTEOSと反応でき、エタノール／TEOSゲルの性質とかなり異なった性質を有する乾燥ゲルを生じる。グリセロール／TEOS基ゲルにおける予想されない性質の変化として、（少なくともほとんどの配合で）一般に次のことが含まれる。

【0046】・過臨界乾燥またはプリ乾燥表面改質を行うことなく低密度を達成できる。

・大幅に簡略化されたエージング。

・触媒を用いないでもゲル化時間が短くなる。

・バルクサンプルの強度が従来のTEOSゲルよりも（所定の密度で）ほぼ一桁の大きさだけ増すこと。

・極めて大きな表面積（～1，000m^2/g）

・バルクサンプルの光学的透明度が高い（これは孔径分布が狭いことによるものである）。

【0047】低密度－－本発明によれば、プリ乾燥表面改質または過臨界乾燥を行うことなく、極めて低密度で乾燥ゲルを形成することが可能である。これら低密度は一般に0．3～0．2g/cm^3（非多孔質のSiO_2は2．2g/cm^3の密度を有する）前後または注意した場合には0．1g/cm^3まで低下できる。多孔率（この多孔率は中空となっている構造の％を意味する）なる用語で記載した場合、この用語は約86％～91％（約95％の多孔率では密度は0．1g/cm^3である）の多孔率を意味する。図3に示されるように、これら多孔率は86％の多孔質に対しては約1．4の誘電率に対応し、91％の対応に対しては1．2の誘電率に対応する。これら高い多孔率を可能とする実際の機構は完全には判っていない。しかしながら、その理由としてゲルが高い機械的強度を有すること、およびゲルが多くの表面OH（水酸）基を有しないこと、これらの組み合わせまたはその他の要因を挙げることができる。この方法ではウェーハ全体に優れた均一性も得られるようである。

【0048】所望すれば、このプロセスは多孔率を90％以上から約50％までにするよう（TEOS／溶剤比を変えることにより）調節できる。小さい孔径を有する代表的な従来の乾燥ゲルは、これら低密度を得るための乾燥前に過臨界乾燥または表面改質工程のいずれかを必要としていた。いくつかの従来のキセロゲルは50％よりも大きい多孔率を有しているが、これら従来のキセロゲルはこれよりもかなり大きい孔径（一般に100nm以上である）を有していた。これら大きな孔径のゲルは機械的強度がかなり低い。更にこれらの大きな孔径により、孔はマイクロ回路上の小さい（一般に1μmより小）のパターン化されたギャップを充填するには不適当となっている。所望すれば、このプロセスは多孔率を50％よりも低くするように（TEOS／溶剤比を変えることにより）調節することも可能である。早期のゲル化を防止するように注意を払えば20％までの多孔率が得られる。

【0049】従って、本発明は新規で簡単なナノ多孔質の低密度誘電体製造方法を可能にした。この新規なグリセロールに基づく方法は過臨界乾燥または乾燥前の表面改質工程を行うことなく、バルクエーロゲルおよび薄膜エーロゲルの双方を製造可能にするものである。従来のエーロゲルは乾燥中の実質的な孔の崩壊を防止するためにこれら工程の少なくとも1つを必要としていた。

【0050】密度の予想－－シリコン（または他の金属）に対するグリセロールの比を変えることにより、乾燥後の密度を正確に予想できる。この正確性は低揮発性グリセロール溶剤により可能とされる良好に制御された蒸発によるものである。本プロセスはエージング中および乾燥中の優れた収縮制御を示すので、このプロセスは乾燥されたゲルの密度（従って多孔率）を正確に予想できる。バルクゲルでは密度予想は一般に大きな問題とは見なされていなかったが、これまで一般に薄膜ゲルの最終多孔質度を予想することは困難であった。このような低多孔率の乾燥ゲルに対しても正確な密度予想ができる

ことは、この新しいプロセスが低多孔率ゲルを形成するための現在のキセロゲルプロセスよりも好ましい１つの理由となっている。

【００５１】簡略化されたエージングーーナノ多孔質の誘電体を製造する際に湿潤ゲル薄膜にエージングとして知られるプロセスを施すことが好ましいことを発見した。加水分解および縮合反応はゲル点で停止せず、反応が目的を果たして停止するまでゲルを再構成し、エージングし続ける。エージング中、固体構造部分の優先的な溶解および再デポジションにより有益な結果が生じる。これら有益な結果には強度が増し、孔径がより均一となり、乾燥中の孔の耐崩壊性が増すことが挙げられる。しかしながら、膜はエージングを生じさせるために所定の時間、かなり一定に保持すべき極めて少量の孔内流体しか含んでいないので、薄膜形成時に湿潤ゲルをエージングすることは困難である。エージングがネットワークを強化する前に膜から孔内流体が蒸発する場合、膜はキセロゲル状に密になる傾向かある。他方、ネットワークが強化される前に雰囲気から薄膜上に過剰の孔内流体が凝縮すると、これによりエージングプロセスが局部的に乱され、膜の欠陥が生じることあがる。

【００５２】我々の新規なグリセロールに基づくプロセスは薄膜ナノ多孔質誘電体のエージングを大幅に簡略化するものである。他の薄膜ナノ多孔質誘電体エージングプロセスは、かなりの蒸発、流体凝縮を可能にするか、または制御されたエージング雰囲気を必要としている。これらグリセロールに基づくプロセスはデポジションおよびゲル化中に少なくともある程度下記に示すエチレングリコールに基づくプロセスを同じように挙動する。しかしながらエチレングリコール基ゲルは一般に室温でもエージング中にかなりの蒸発を防止するため、一般に雰囲気制御を必要とする。これと対照的にグリセロール基ゲルはエージング中の蒸発および収縮レートを大幅に低下している。これによりエージング中の雰囲気制御を緩めたり、省略することが可能となっている。我々は室温または高温エージング中に受動的な雰囲気制御を行うだけで高品質の薄膜グリセロール基ナノ多孔質誘電体を製造できる。

【００５３】より短いゲル時間ーーグリセロールの使用によりゲル時間もかなり短縮される。代表的な多くのエタノール基前駆物質は触媒の作用を受けた時は少なくとも４００秒のゲル時間を有する（油中水触媒作用ではもっと長い）。しかしながら、触媒作用がなくてもある種のグリセロール基前駆物質はウェーハにスピンオンする間ゲル化することを発見した。このような迅速なゲル化はエタノール基ゲルよりも高速であるだけでなくエチレングリコール基ゲルよりもかなり高速である。図４は使用したアンモニア触媒に応じた２つの異なるエチレングリコール基組成物のゲル時間を示す。これらゲル時間は薄膜の場合のようなエタノールおよび／または水の蒸発がないバルクゲルの場合のものである。蒸発はシリカの量を増すのでゲル時間を短くする。従って、これらゲル時間は所定の前駆物質／触媒に対する上限となり得る。図４に示されているゲル時間は従来のエタノール基前駆物質のゲル時間よりもほぼ短くなっている。一般にゲル時間はアンモニア触媒の濃度に対し一次の従属性も示す。このことはゲル時間を容易に制御できることを意味している

【００５４】これら新規なグリセロール基ゲルの薄膜ではゲル化用触媒を用いなくても数秒内で常にゲル化できる。我々は触媒を添加しなくても薄膜内でゲル化を開始するのに使用できるいくつかのメカニズムを解明した。１つの方法は揮発性溶剤を蒸発させることにより前駆物質ゾルを濃縮することである。他の方法は、前駆物質ゾル内の酸を蒸発させることによりｐＨを増加することである。このような蒸発による塩基化はゲル化の開始を助けるよう、前駆物質ゾルのｐＨを高めることに依存している。しかしながらこの塩基化プロセスは一般に７より低い値から７より高い値までのｐＨの変更を必要としない。このような蒸発による塩基化は代表的な塩基性触媒反応プロセスと同様に作用するので、ゲル化を大幅にスピードアップする。常温および常圧ではある種の酸、例えば硝酸はエタノールに匹敵する蒸発レートを有する。高揮発性溶剤および／または安定化用酸の濃度および／またはタイプを変えることによりゲル化時間を調節するための簡便な極めてフレキシブルな方法が得られる。

【００５５】より高い強度ーーグリセロール基サンプルの性質は乾燥収縮率の低い場合、および湿潤ゲルと乾燥ゲルの定量的な取り扱い性の差の双方で判るように、通常のゲルとはかなり異なるようである。従って、物理的な検査をするとグリセロール基乾燥ゲルは従来のゲルおよびエチレングリコール基乾燥ゲルの双方と比較して機械的性質が改善されているように見える。図５はエチレングリコール基ゲルと従来のエタノール基乾燥バルクゲル（双方は同じ初期密度を有する）を使用して調整された１つのサンプルの等温圧縮測定中に測定された体積弾性率を示す。構造の座屈に寄与する初期変化の後に双方のサンプルは弾性率が密度に指数法則に従って従属することを示す。この指数級数の従属性は通常乾燥ゲルで観察されるものである。しかしながら、驚くことは、エチレングリコール基乾燥ゲルの強度である。所定の密度（従って誘電率）においてエチレングリコール乾燥ゲルのこのサンプルの弾性率は従来の乾燥ゲルよりも一桁大きい。先の評価により、グリセロール基ゲルはエチレングリコール基ゲルよりも強度が強いことが判る。これら評価には定性的な取り扱いテストおよび乾燥中の収縮に基づく情報がある。この強度が増加する理由については全く明らかでない。しかしながら、先の実験によれば、ゲル化時間が短いことおよび／または孔径分布が狭いことが、この高強度の理由であることが判る。

【００５６】大きな表面積——我々はいくつかの乾燥バルクゲルの表面積を測定した。これら表面積は６００～８００m^2／ｇの範囲内の表面積を有する代表的エタノール基乾燥ゲルと比較して１０００m^2／ｇの大きさであった。このように、表面積が大きいことは孔径が小さく、機械的性質が改善されていることを意味する可能性がある。現時点ではグリセロール基乾燥ゲルでこれら表面積が大きい理由は不明である。

【００５７】孔径分布——これら乾燥バルクゲルの光学的透明度は、以前に製造したこの密度でのエタノール基乾燥ゲルよりも高かった。このように光学的透明度が優れているのは孔径分布が極めて狭いことによるものである可能性がある。しかしながらグリセロールがこのような効果を有する理由は不明である。以前の実験では、ゲル化時間が短いことと、孔径分布が狭いことが関連しているという１つの可能性のある説明が示されている。図６は約０．５７ｇ／cm^3の密度を備えたバルクゲルサンプルの（ＢＪＨ脱着測定により測定された）孔径分布を有する。このサンプルの平均孔径（脱着法則）は３．７６ｎｍであった。代表的な孔は真に円筒形ではないので、本明細書で使用する径は、実際には容積に対する全ゲル表面積の比と同じ容積に対する表面積比を有する等価的円筒体の径を示す。

【００５８】上に示したようにグリセロール基ゲルのある性質はバルクゲルおよび薄膜の双方に当てはまる。しかしながら、半導体ウェーハ上のナノ多孔質誘電体フィルムのような薄膜に当てはめた時、いくつかの利点が最も明らかとなる。最も重要な利点とは、この新規な方法によりデポジション中またはゲル化中に雰囲気制御を行うことなく高品質のナノ多孔質膜を処理できるということである。

【００５９】雰囲気制御をすることなくナノ多孔質の薄膜をデポジットし、ゲル化できることは重要であるが、雰囲気制御を行うことなくナノ多孔質の薄膜をエージングすることも好ましい。これにより、デポジション法よりもより大きな挑戦が可能となったことが判った。この主な理由は、デポジションおよび常温でのゲル化は数分または数秒でも生じ得るが、常温でのエージングは一般に数時間必要であるからである。従って、短いプロセスで許容可能な収縮を生じさせる蒸発レートは、プロセス時間を一桁長くした場合に許容できない収縮を生じさせる可能性がある。

【００６０】一例として、あるグリセロール基ゲルを用いると常温で満足できるエージングの大きさは１日の長さであることを発見した。しかしながら、より高い温度を用いると数分の長さの時間で薄膜をエージングできることを図１は示している。これらエージング時間は多数の代表的なエージング基ゲルおよびエチレングリコール基ゲルの好ましいエチレン時間に匹敵する。従って、これら時間および温度を図１、図７および図２の蒸発レートと組み合わせると、表２に示されるようなエージング中の概略的な厚みの損失を生じさせる。これら予想される厚み損失は、特に薄膜に用いる場合の許容可能な厚み損失と比較する必要がある。許容可能な厚み損失の確かなガイドラインは存在していないが、ナノ多孔質誘電体のようなあるマイクロ回路用の１つの提案されるガイドラインは、厚み損失を膜厚の２％よりも少なくすべきであるということである。１μｍの仮説的な公称膜厚（実際の膜厚は０．５μｍよりもかなり小さい値から数μｍまで変わり得る）に対しては、許容可能な厚さ損失は２０ｎｍであることが示される。図２に示されるように、グリセロール基は常温での雰囲気制御をすることなく、このような先の目的を達し得る。従って、本発明は雰囲気制御をすることなく、多孔率が制御された薄膜ナノ多孔質アエロゲルをデポジットし、ゲル化し、エージングし、乾燥可能にするものである。別の特徴によれば、本発明はエージングチャンバーの容積を制限するような受動的な雰囲気制御だけで、多孔率が制御された薄膜ナノ多孔質エーロゲルをデポジットし、ゲル化し、高温で高速エージングし、乾燥可能にするものである。

【００６１】

【表１】

ある薄膜グリセロール基における温度に従属した概略的エージング時間

エージング温度（℃）	グリセロール基ゲルのエージング時間（概略値）
２５	１日
１００	５分
１４０	１分

【００６２】

【表２】

エージング中の概略厚み損失対飽和率

エージング時間／温度	エージング中の厚み損失								
	エタノール基ゲル			ＥＧ基ゲル			グリセロール基ゲル		
	%飽和			%飽和			%飽和		
	0%	50%	99%	0%	50%	99%	0%	50%	99%
1日／25° C	8 mm	7 mm	86 μm	17 μm	7 μm	172 nm	13 nm	5 nm	.1 nm
300秒／100° C	—	—	—	3 μm	1.2 μm	90 nm	600 nm	420 nm	9 nm
60秒／140° C	—	—	—	—	—	—	6 μm	3 μm	60 nm

【００６３】改善された歩留まりおよび信頼性を検討するには、２%以下の損失、例えば０．５%または０．１%より低い厚み損失が必要である。受動的な雰囲気制御を使用することにより、本発明はこれら値まで、更に低い蒸発損失まで拡張できる。このような受動的制御は少なくともエージング中に比較的小さい密閉された容器内にゲルを入れることである。本発明のこのような特徴によれば、ウェーハからの蒸発が密閉容器内の雰囲気の飽和比率を上げるように作用する。所定の温度では、液体の蒸気圧に等しくなるよう、蒸気の部分圧が十分に高くなるまでこの蒸気が続く。従って、低い蒸気圧での溶剤と温度の組み合わせは、より高い蒸気圧の組み合わせで可能な量と同じ量の液体溶剤を蒸発させることはできない。図８は数種の溶剤において蒸気圧がどのように温度と共に変化するかを示している。図９はウェーハと同じ径の５ｍｍ高さの円筒形容器内に７０%多孔質のゲルを入れた場合、溶剤から成るどれだけ厚い層を潜在的に蒸発できるかの予想値を示している。図１０はウェーハ上に１ｍｍ高さの空気スペースがある容器での同様な予想値を示す。これら図は、５ｍｍ高さの空気スペースがある場合、グリセロール基ゲルでは１２０℃まで、エチレングリコール基ゲルでは５０℃まで、２０ｎｍの先の目標を達成できることを示している。１ｍｍ高さの空気スペースではグリセロール基ゲルでは１５０℃までずっと、エチレングリコール基ゲルでは８０℃まで、２０ｎｍの目標が達成できる。当然ながら、より低い温度の処理では蒸発を少なくすることが可能である。１ｍｍの容器を使用した受動的蒸発制御によれば、１００℃でもグリセロール基ゲルでは厚み損失を１ｎｍよりも少なく（１μｍ厚の膜では０．１%）することが可能である。

【００６４】このような受動的制御方法には種々の変形例がある。１つの変形例は容器のサイズを大きくできる。厚み損失は容器の容積と共に線形的に増加する。しかしながら、１０００ｃｍ　の容積でも８０℃でわずか５ｎｍだけグリセロールを蒸発できる。別の変形例は、ゲルの多孔率を制御することである。すなわちより高い多孔率のゲルは一般に厚み損失が大きいが、より低い多孔率のゲルは一般に厚み損失が少ない。

【００６５】グリセロールの１つの欠点は、粘性が比較的高いことにあり、このことはギャップ充填および／または平面化による問題を生じさせ得る。上記のように粘性を下げるには、低粘性の高揮発溶液を使用できる。図１１Ａは常温でのエタノールとグリセロールの混合物およびメタノールとグリセロールの混合物の計算された粘性を示す。図に示されるようにアルコールはこれら混合物の粘性を大幅に下げることができる。図１１Ｂは常温でのエタノールとエチレングリコールの混合物およびメタノールとエチレングリコールの混合物の計算された粘性を示す。図面が示すようにエチレングリコールはグリセロールよりも粘性が小さく、少量のアルコールでもこれら混合物の粘性を大幅に下げる。また、原液内にエタノールを使用する粘性が所望の粘性よりも高ければ、前駆物質溶液内にメタノールを使用することにより更なる改善を実現できる。図１１Ａ～１１Ｂに示された粘性は純粋な液体混合物だけに対するものである。実際には膜前駆物質溶液に応じて前駆物質溶液はグリセロール、アルコール、水、酸および一部が反応している金属アルコキシドを含むことがある。当然ながら、縮合反応に触媒作用することによりデポジット前に粘性を増加できるので、図１１Ａ～１１Ｂに示されている値は低い方の限界を示している。

【００６６】このようなマルチ溶剤方法は別の方法と組み合わせてもよいし、別の方法に変えることができる。このような別の方法とは、使用中のゾル粘性を小さくするよう、高温を使用する方法である。デポジション中に前駆物質を加熱し、および／または希釈することにより（例えば転送ラインおよびウェーハスピンステーションのデポジションノズルを加熱することにより）、前駆物質ゾルの粘性を実質的に下げることができる。このような予熱はゾルの粘性を下げるだけでなく、ゲル時間もスピードアップし、高揮発性溶剤の蒸発も加速する。また、ウェーハも予熱することも好ましい。このようなウ

ェーハの予熱を行うには、プロセス制御を改善しなければならず、特に粘性のより大きい前駆物質の場合のギャップ充填を改善できる。しかしながら、多くの使用例では予熱は不要であるのでプロセスフローが簡略化される。このようなウェーハ予熱をしないスピンオン方法を用いる場合、スピンステーションは温度制御スピナーを必要としない。

【００６７】このような簡単な薄膜アエロゲル製造プロセスで製造された乾燥ゲルは、多くの用途に使用できる。これら用途のいくつかは従来の方法を使う場合のようにコスト的に有効ではない。これらの用途として（特に半導体基板上に設けられた）低誘電率の薄膜、小型化学センサー、断熱構造および断熱層（赤外線検出器のための熱分離方法を含む）が挙げられる。一般的に多くの低誘電率の薄膜は６０％よりも大きい多孔率を必要とし、重要な応用例では８０または９０％よりも大きい多孔率を必要とするので、誘電率はかなり低下する。しかしながら構造上の強度および完全性の要因は、実際的な多孔率をわずか９０％に制限し得る。熱分離構造および熱分離層を含むいくつかの応用例は、強度および剛性を高くするためにある程度の多孔率を犠牲にする必要がある。これらより高い剛性の条件は３０または４５％程度に低い多孔率の誘電体を必要とする。他の高強度／靭性の応用例、特に密度よりも表面積が重要なセンサーでは、多孔率が２０～４０％の間の低多孔率ゲルを使用することが好ましいことがある。

【００６８】上記薄膜の説明はマイクロ電子回路用の薄膜アエロゲルの周辺に話題を集中している。しかしながらアエロゲルは他の用途、例えば受動的基板上に設けられた薄膜にも有効である。これらの新規な高強度の製造が容易なゲルは、これら用途の多くを実用化するものである。このような用途の目的のためには受動的基板はマイクロ電子回路を含まないか、または含むか、または少なくともアエロゲルと電子回路との間に相互作用のない基板として定義される。Ｃ．Ｊ．ブリンカーおよびG．W．シェーラーによる「ゾルーゲル化学」は第１４章においてこれら用途のいくつかについて述べている。これら受動的な用途の一部にはある種の工学的コーティング、ある種の保護用コーティングおよびある種の多孔質コーティングが含まれる。

【００６９】反射防止（ＡＲ）コーティングは広範な多孔率を必要とする。これらコーティングは一般に２０％の多孔率から７０％の多孔率まで変化するが、適当な表面保護をする場合、より高い多孔率（９０％以上）が有効であり、高性能のコーティングまたは高屈折率の基板に設けられたコーティングではより低い多孔率（１０％まで、またはそれ以下）を使用できる。ある単一層の反射防止コーティングでは、３０～５０％の間の多孔率を有するゲルを使用することが望ましい。高性能のマルチ層反射防止コーティングは基板に隣接するより密度の高い層（例えば１０～３０％の多孔率）、および空気境界部に隣接するより密度の低い層（例えば４５～９０％の間の多孔率）を必要とする。特に高強度および表面積が主目的である場合のより高い強度／靭性の用途では、２０～４０％の間の多孔率を備えた低多孔率ゲルを使用することが望ましい。その他の薄膜皮膜は最も低い密度を必要とし得るので、８５％、９０％または９５％よりも大きい多孔率を必要とする。

【００７０】これら新規な高強度の製造の容易なアエロゲルから利益が得られるバルクゲルの用途も多数ある。これらバルクゲルの用途としてはナノ多孔質（すなわち分子）ふるい、断熱材、触媒支持体、吸着剤、音響絶縁体、光分離膜があるが、これらのみに限定されるものではない。一般的に多くのバルク用途では６０％よりも大きい多孔率を必要とし、重要な用途では８０％または９０％よりも大きい多孔率を必要とする。しかしながら、構造上の強度および完全性の要因は実用的な多孔率をわずか９５％に制限し得る。ある用途（ふるいを含む可能性がある）は、高強度および靭性のために多孔率を犠牲としなければならないことがある。これらより高い靭性の条件は３０または４５％もの低い多孔率を有する誘電体を必要とし得る。密度よりも表面積のほうがより重要である他の高強度／靭性用途（触媒支持体およびセンサーを含む可能性がある）では、２０～４０％の多孔率を有する低多孔率のゲルを使用することが望ましい場合がある。

【００７１】代表的なゾルーゲル薄膜プロセスは乾燥時に崩壊し、密になるゲルを製造し、よって制限された多孔率（大きな孔径の場合には６０％まで、一般に当該孔径では実質的に５０％よりも小さい）を有するキセロゲルを形成する。キセロゲル膜の形成の制御しない乾燥条件下では内側の孔の多くは永久的に崩壊する。しかしながら、薄膜アエロゲル形成時には最終密度に影響するエージングおよび／または乾燥中の収縮が少量であっても、ほぼ無崩壊状態のままである。

【００７２】次に図１２Ａを参照する。この図には（一般的にウェーハ形状の）半導体基板１０が示されている。一般的な基板はシリコン、ゲルマニウムおよびヒ化ガリウムから成り、基板はアクティブデバイス、低レベルの配線および絶縁層および当業者に知られている図示されていない他の多くの一般的構造を含むことができる。基板１０上には数本のパターン形成された導線１２（Ａｌ－０．５％のＣｕ組成物から成る）が示されている。これら導線１２は所定幅（一般に１ミクロンの何分の１か）のギャップ１３によって分離されるように、その長さの少なくとも一部にわたって平行に延びる。導線およびギャップの双方は図示されているものよりも大きい高さ対幅比を有することができ、一般にデバイスの大きさが小さくなればなるほどこの比は大きくなる。

【００７３】本発明の第１の実施例によれば、６１．０

ｍｌのテトラエトキシシラン（ＴＥＯＳ）と、６１．０ｍｌのグリセロールと、４．８７ｍｌの水と、０．２ｍｌの１ＭのＨＮＯ$_3$とを混合し、～６０℃で１．５時間還流し、原液を形成する。これと等価的に表現すれば、０．２７モルのＴＥＯＳと、０．８４モルのグリセロールと、０．２７モルの水と、２．０４Ｅの４モルのＨＮＯ　を混合し、～６０℃で１．５時間還流する。原液を冷却した後、溶液をエタノールで希釈し、粘性を低下してもよい。適当な原液と溶剤との容積比は１：８である。しかしながらこの比は所望する膜厚、スピン速度および基板に応じて変わる。これを強く混合し、一般に～７℃で冷蔵庫に保管し、使用するまで安定性を維持する。この液は一般にフィルムデポジション前に常温まで温められる。基板１０上に常温で３～５ｍｌのこの前駆物質ゾルを分配し、基板１０を約５～１０秒の間、１５００～５０００ｒｐｍ（この速度は所望する膜厚に応じて決まる）でスピニングし、ゾルの薄膜１４を形成する。このデポジションは溶剤の飽和度を特別に制御しない雰囲気内（例えば新型でない湿度制御装置を備えたクリーンルーム内で）実行できる。このデポジションおよびスピニング中、およびこれら工程の後では、膜１４からエタノール、水、硝酸が蒸発するが、グリセロールの揮発性は低いのでグリセロールの実質的な蒸発は生じない。このような蒸発は薄膜を一次的に冷却するが、膜の温度は蒸発レートが低下した後に数秒内に上昇する。この冷却は制約されるが、ゲル化を防止するものではない。この蒸発は薄膜１４を収縮させ、ゾル内のシリカ量を濃縮し、薄くされた膜１８を形成する。図１２Ｂは実質的にすべての（約９０％またはそれ以上の）エタノールが除かれた後に得られる薄くされたゾル膜１８を示している。このような膜の濃縮、蒸発による塩基化および／または再加熱は一般に数秒内のゲル化を生じさせる。

【００７４】膜１８はゲル点における孔内流体に対するシリコンの概略的に知られている比を有する。この比は（残りの水、継続する反応および付随的に生じる蒸発によりわずかに変化がある）デポジット当初のゾル内のグリセロールに対するＴＥＯＳの比にほぼ等しい。この方法は主にゲルが永久的に崩壊するのを防止するので、この比はゾル薄膜から製造されるアエロゲルの密度を決定する。

【００７５】ゲル化後、薄膜の湿潤ゲル１８は多孔質の固体および孔内流体を含み、１つ以上の制御された温度で時間をかけてエージングすることが好ましい。例えば常温で約１日かけてエージングすることが好ましい。孔内流体は処理中に多少変わることに留意すべきである。このような変化は継続する反応、蒸発／凝縮または薄膜への化学的添加物に起因するものである。エージングは約２５℃で約２４時間の間、基板およびゲルを放置するか、またはこれらを密閉された容器内に約１分の間、１３０～１５０℃に加熱することによって達成することが好ましい。

【００７６】過臨界的流体抽出を含むいくつかの方法のうちの１つにより、実質的に密度を高めることなくエージングされた膜１８を乾燥できる。しかしながらこれら新規なグリセロール基ゲルを用いる場合、別の方法として溶剤交換法を使用し、エージング流体を乾燥流体に置換し、次にこの乾燥流体からの膜１８を空気乾燥する方法がある。この乾燥方法はエージング流体を別の流体に置換する溶剤交換法を利用するものである。この流体がエージング流体と同一であるか、またはそうでないかに拘わらず、乾燥中に存在する孔内流体のことを乾燥流体と称すことが多い。この乾燥流体を用いる場合、溶剤交換法はグリセロールおよびそれに関連する高表面張力が支配的なエージング流体を表面張力のより低い乾燥流体で置換する。この溶剤交換法は１工程または２工程プロセスとして実行できる。２工程プロセスでは第１の工程でエージングされた薄膜１８上に常温の（またはこれよりも温度の高い）約３～８ｍｌのエタノールを分配してエージング流体を中間流体に置換し、次に約５～１０秒の間、約５０～５００ｒｐｍの間でウェーハをスピニングする。エージング流体のほとんどを置換するには３回～６回のスピンオンシーケンスが必要であることが多い。第２の工程では中間流体をヘプタンのような乾燥流体で置換することが好ましい。この第２工程はエージングされた薄膜１８上に常温（またはそれより高い温度）の約３～８ｍｌのヘプタンを分配し、次に約５～１０秒の間、５０～５００ｒｐｍの間でウェーハをスピニングすることから成る。中間流体のほとんどを置換するには３回～６回のスピンオンシーケンスが必要であることが多い。この溶剤交換法により我々は乾燥前にほとんどすべてのグリセロール含有流体を除くことが可能となる。この乾燥流体（本例ではヘプタン）は最終的に湿潤ゲル１８から蒸発され、乾燥されたナノ多孔質の誘電体（乾燥ゲル）が形成される。エージング流体に可溶性のある液体から満足できる状態で膜を乾燥できれば中間流体は不要となる。多くの場合、エタノールまたは他の適当な溶剤から湿潤ゲルを乾燥できる。

【００７７】この蒸発は乾燥流体でほとんど飽和されていない雰囲気にウェーハ表面を暴露することによって実行できる。例えばウェーハは実質的に制御されていない雰囲気内に入れることができるし、また雰囲気内に乾燥ガスを導入できる。沸騰を防止するには乾燥流体の沸点よりも多少低い温度、例えば常温で乾燥を開始するべきである。グリセロールのような沸点のより高い乾燥流体を使用する場合（例えば溶剤の交換を行わない乾燥の場合）、乾燥開始温度はエージング温度の近くか、それに等しい温度まで高めることができる。薄膜は（一般に数秒内で）圧倒的な乾燥状態となるので、温度はエージング流体温度乾燥流体の双方の沸点よりも高くしなければならない。この方法は破壊的な沸騰を防止し、すべての

流体を除去できるようにする。グリセロールのみならずその他のある種の流体は、これら流体が沸騰するほぼ同じ温度で分解するか、または沸騰する変わりに分解する。これら流体、特に分解して有害物質となり得るようなグリセロールのような流体を使用する場合、蒸発した流体または乾燥していないウェーハを過熱しないように注意しなければならない。乾燥後は残留物質、例えば誘電体内またはその上に存在する有機物を除去するのを助けるよう、短時間の間でナノ多孔質誘電体を（例えば１５～６０分の間で３００℃で）ベークすることが好ましい。この実施例の（表面改質前の）理論的な誘電率は１：３である。

【００７８】誘電率を下げるには乾燥したゲルをデヒドロキシル化（アニール）することが好ましい。これはヘキサメチルジシラザン（ＨＭＤＳ）またはヘキサフェニールジシラザン蒸気のような薬剤を備えた乾燥雰囲気内にウェーハを入れることによって実行できる。このＨＭＤＳはほとんどの水および／または乾燥ゲルの孔の表面に結合したヒドロキシル基をメチル基に置換する。このような置換は常温またはそれよりも高い温度で実行できる。このような置換は水および／またはヒドロキシル基を除くだけでなく、乾燥したゲルを疎水性（水反撥性）にできる。ヘキサフェニールジシラザンは水および／またはヒドロキシル基も除き、乾燥したゲルを疎水性にする。しかしながら、フェニール基は誘電率を若干高くすることを犠牲にして、メチル基よりもより高い温度の安定性を有する。

【００７９】図１３は、本発明の一実施例による前駆物質ゾルからエーロゲル薄膜を得るための一般的な方法のフローチャートを示す。表３および４は、この方法で使用される物質の一部の概要である。

【００８０】

【表３】

物質の概要

参照番号	特定例	機能の説明	好ましい代替物
１０ ２６	シリコン	基板	半導体基板、Ge、GaAs、アクティブデバイス、低レベル層、ガラス、プラスチック、光学的基板
１２	Al-0.5%Cr	パターン化された導線	Al、Cu、その他の金属、ポリシリコン
	ＴＥＯＳ	前駆物質ゾル反応体	その他のシリコン基金属アルコキシド(TMOS 、（TMOS, MTEOS, BTMSE等）、その他金属のアルコキシド、粒状金属酸化物、有機前駆物質およびそれらの組み合わせ
	グリセロール	前駆物質ゾルの第１溶剤（低揮発性）	エチレングリコール、三価アルコール、グリセロールと二価および／または三価アルコールとの組み合わせ、1,4-ブチレングリーコールおよび1,5-ペンタンジオール、1,2,4-ブタントリオール；1,2,3-ブタントリオール；2 メチル- プロパントリオール；および2-(ヒドロキシメチル)-1,3-プロパンジオール；1-4,1-4,ブタンジオール；および2-メチル-1,3- プロパンジオール
	硝酸 (HNO_3)	前駆物質ゾルの安定剤	その他の酸

【００８１】

【表４】

物質の概要

参照番号	特定例	機能の説明	好ましい代替物
	エタノール	前駆物質ゾルの第2溶剤（高揮発性）	メタノール、その他のアルコール
	エタノール	粘性低減溶剤	メタノール、その他のアルコール
	水酸化アンモニウム	ゲル化触媒	アンモニア、揮発性アミン種、揮発性塩素種およびデポジットされたゾルのpHを上げるその他化合物
	ゲル状にされた当初の孔内流体	エージング流体	グリセロール、エチレングリコール、水、エタノール、その他アルコール、それらの組み合わせ
	エージング流体	乾燥流体	加熱されたエージング流体、ヘプタン、アセトン、イソプロパノール、エタノール、メタノール、2-エチルブチルアルコール、アルコールと水の混合物、エチレングリコール、エージング流体と混和し、エージング流体よりも表面張力の低いその他液体、それらの組み合わせ
	ヘキサメチルジシラザン（HMDS）	表面改質剤	ヘキサフェニールジシラザン、トリメチルメトキシシラン、ジメチルジメトキシシラン、トリメチルクロロシラン（TMCS）、フェニール化合物およびフルオロカーボン化合物

【００８２】本発明の第２のより高い密度の実施例によれば、１５０．０ｍｌのテトラエトキシシラン（ＴＥＯＳ）と、６１．０ｍｌのグリセロールと、１５０．０ｍｌのエタノールと、１２．２ｍｌの水と、０．４８ｍｌの１ＭのHNO_3とを混合し、～６０℃で１．５時間還流し、原液を形成する。これと等価的に表現すれば、０．６７モルのＴＥＯＳと、０．８４モルのグリセロールと、２．５７モルのエタノールと、０．６７モルの水と、４．９０Ｅの４モルのHNO_3を混合し、～６０℃で１．５時間還流する。原液を冷却した後、溶液をエタノールで希釈し、粘性を低下してもよい。適当な原液と溶剤との容積比は１：８である。これを強く混合し、一般に～７℃で冷蔵庫に保管し、使用するまで安定性を維持する。この液は一般にフィルムデポジション前に常温まで温められる。基板１０上に常温で３～５ｍｌのこの前駆物質ゾルを分配し、基板１０を約５～１０秒の間、１５００～５０００ｒｐｍ（この速度は所望する膜厚に応じて決まる）でスピニングし、ゾルの薄膜１４を形成する。このデポジションは溶剤を制御しない雰囲気内（例えば新型でない湿度制御装置を備えたクリーンルーム内の標準的排気内）で実行できる。このデポジションおよびスピニング中、およびこれら工程の後では、膜１４からエタノール（ＴＥＯＳおよび水からの粘性低下添加剤および反応生成物）および水が蒸発するが、グリセロールの揮発性は低いのでグリセロールの実質的な蒸発は生じない。このような蒸発は薄膜１４を収縮し、ゾルのシリカ成分を濃縮し、薄くされた薄膜１８を形成する。図１２Ｂは実質的にすべての（約９５％またはそれ以上の）水が除かれた後に得られる薄くされたゾル膜１８を示している。このような膜の濃縮により、一般に数分内でゲル化が生じる。

【００８３】第１実施例に記載のプロセスの後に、一般に次のような処理が続く。ゲル化後、薄膜の湿潤ゲル１８は多孔質の固体および孔内流体を含み、１つ以上の制御された温度で時間をかけてエージングすることが好ましい。過臨界流体抽出を含むいくつかの方法のうちの１つにより、実質的に密度を高めることなくエージングされた膜１８を乾燥できる。しかしながらこれら新規なグリセロール基ゲルのより低い密度の配合を用いる場合、非過臨界的乾燥、例えば溶剤交換を行い、その後、第１

実施例に記載のように乾燥流体から膜を乾燥することが好ましい。このナノ多孔質誘電体は次に第１実施例に記載のように、乾燥のベーキングおよび／または表面改質処理を行うことができる。この実施例の（表面改質前の）理論的誘電率は１．６である。

【００８４】本発明の第３のより高い密度の実施例によれば、２０８．０ｍｌのテトラエトキシシラン（ＴＥＯＳ）と、６１．０ｍｌのグリセロールと、２０８．０ｍｌのエタノールと、１６．８ｍｌの水と、０．６７ｍｌの１ＭのHNO_3とを混合し、～６０℃で１．５時間還流し、原液を形成する。これと等価的な表現をすれば、０．９３モルのＴＥＯＳと、０．８４モルのグリセロールと、３．５６モルのエタノールと、０．９３モルの水と、６．８０Ｅの４モルのHNO_3を混合し、～６０℃で１．５時間還流する。原液を冷却した後、溶液をエタノールで希釈し、粘性を低下してもよい。適当な原液と溶剤との容積比は１：８である。これを強く混合し、一般に～７℃で冷蔵庫に保管し、使用するまで安定性を維持する。この液は一般にフィルムデポジション前に常温まで温められる。基板１０上に常温で３～５ｍｌのこの前駆物質ゾルを分配し、基板１０を約５～１０秒の間、１５００～５０００ｒｐｍ（この速度は所望する膜厚に応じて決まる）でスピニングし、ゾルの薄膜１４を形成する。このデポジションは溶剤を制御しない雰囲気内（例えば新型でない湿度制御装置を備えたクリーンルーム内の標準的排気内）で実行できる。このデポジションおよびスピニング中、およびこれら工程の後では、膜１４からエタノールおよび水が蒸発するが、グリセロールの揮発性は低いのでグリセロールの実質的な蒸発は生じない。このような蒸発は薄膜１４を収縮し、ゾルのシリカ成分を濃縮し、薄くされた薄膜１８を形成する。図１２Ｂは実質的にすべての（約９５％またはそれ以上の）水が除かれた後に得られる薄くされたゾル膜１８を示している。このような濃縮により、一般に数分内でゲル化が生じる。

【００８５】第１実施例に記載のプロセスの後に、一般に次のような処理が続く。ゲル化後、薄膜の湿潤ゲル１８は多孔質の固体および孔内流体を含み、１つ以上の制御された温度で時間をかけてエージングすることが好ましい。約２４時間装置を２５℃とすることによりエージングを達成できる。過臨界流体抽出または溶剤交換およびその後に行われる空気乾燥を含むいくつかの方法のうちの１つにより、実質的に密度を高めることなくエージングされた膜１８を乾燥できる。しかしながらこれら新規なグリセロール基ゲルのより高い密度の配合を用いる場合、エージング流体から膜１８を空気乾燥することが好ましい。このような直接乾燥方法では乾燥流体によってほとんど飽和されていない雰囲気にウェーハ表面を暴露する。簡単な方法としては低容積エージングチャンバーからカバーを除き、ゲル表面を実質的に制御されていない雰囲気に暴露する方法がある。別の方法は、エージングチャンバーすなわち雰囲気内に乾燥ガスを導入する方法である。このような直接乾燥方法では、開始開始温度をエージング温度近くまたはそれに等しい温度までに高めることができることが好ましい。このような高温乾燥は表面張力およびそれに関連する収縮を減少し、乾燥をスピードアップし、処理を簡略にする。薄膜は（一般に高温乾燥の場合は数秒内で）圧倒的に乾燥状態となるので、温度はエージング流体および乾燥流体（これら流体は同一流体であることが多い）の双方の沸点よりも高くしなければならない。この方法は、破壊的な沸騰を防止し、すべての流体が除かれるのを保証する。この方法の乾燥流体は有害物質に分解されることがあるグリセロールを含むので、蒸発流体または未乾燥のウェーハを過熱しないように注意しなければならない。次に、第１実施例に記載のように、ナノ多孔質誘電体を乾燥後のベーキングおよび／または表面改質工程を施すことができる。この実施例の（表面改質前の）理論的な誘電率は１．７０である。

【００８６】本発明の第４実施例によれば、２７８．０ｍｌのテトラエトキシシラン（ＴＥＯＳ）と、６１．０ｍｌのグリセロールと、２７８．０ｍｌのエタノールと、２２．５ｍｌの水と、０．９０ｍｌの１ＭのHNO_3とを混合し、～６０℃で１．５時間還流し、原液を形成する。これと等価的な表現をすれば、１．２５モルのＴＥＯＳと、０．８４モルのグリセロールと、４．７６モルのエタノールと、１．２５モルの水と、９．１Ｅの４モルのHNO_3を混合し、～６０℃で１．５時間還流する。原液を放置して冷却した後、溶液をエタノールで希釈し、粘性を低下してもよい。適当な原液と溶剤との容積比は１：８である。これを強く混合し、一般に～７℃で冷蔵庫に保管し、使用するまで安定性を維持する。この液は一般にフィルムデポジション前に常温まで温められる。基板１０上に常温で３～５ｍｌのこの前駆物質ゾルを分配し、基板１０を約５～１０秒の間、１５００～５０００ｒｐｍ（この速度は所望する膜厚に応じて決まる）でスピニングし、ゾルの薄膜１４を形成する。このデポジションは溶剤を制御しない雰囲気内（例えば新型でない湿度制御装置を備えたクリーンルーム内の標準的排気内）で実行できる。このデポジションおよびスピニング中、およびこれら工程の後では、膜１４からエタノールおよび水が蒸発するが、グリセロールの揮発性は低いのでグリセロールの実質的な蒸発は生じない。このような蒸発は薄膜１４を収縮し、ゾルのシリカ成分を濃縮し、薄くされた薄膜１８を形成する。図１２Ｂは実質的にすべての（約９５％またはそれ以上の）水が除かれた後に得られる薄くされたゾル膜１８を示している。このような膜の濃縮により、一般に数分内でゲル化が生じる。

【００８７】第３実施例に記載のプロセスの後に、一般

に次のような処理が続く。ゲル化後、薄膜の湿潤ゲル１８は多孔質の固体および孔内流体を含み、１つ以上の制御された温度で時間をかけてエージングすることが好ましい。過臨界流体抽出を含むいくつかの方法のうちの１つにより、実質的に密度を高めることなくエージングされた膜１８を乾燥できる。しかしながら第３実施例に記載のように、エージング流体から膜１８を空気乾燥することが好ましい。このナノ多孔質誘電体は次に第１実施例に記載のように、乾燥のベーキングおよび／または表面改質処理を行うことができる。この実施例の（表面改質前の）理論的誘電率は１．９６である。

【００８８】本発明の第５実施例によれば、６０９．０ｍｌのテトラエトキシシラン（ＴＥＯＳ）と、６１．０ｍｌのグリセロールと、６０９．０ｍｌのエタノールと、４９．２ｍｌの水と、１．９７ｍｌの１ＭのＨＮＯ$_3$とを混合し、～６０℃で１．５時間還流し、原液を形成する。これと等価的な表現をすれば、２．７３モルのＴＥＯＳと、０．８４モルのグリセロールと、１０．４モルのエタノールと、２．７３モルの水と、２．００Ｅの３モルのＨＮＯ$_3$を混合し、～６０℃で１．５時間還流する。原液を放置して冷却した後、溶液をエタノールで希釈し、粘性を低下してもよい。適当な原液と溶剤との容積比は１：８である。これを強く混合し、一般に～７℃で冷蔵庫に保管し、使用するまで安定性を維持する。この液は一般にフィルムデポジション前に常温まで温められる。基板１０上に常温で３～５ｍｌのこの前駆物質ゾルを分配し、基板１０を約５～１０秒の間、１５００～５０００ｒｐｍ（この速度は所望する膜厚に応じて決まる）でスピニングし、ゾルの薄膜１４を形成する。このデポジションは溶剤を制御しない雰囲気内（例えば新型でない湿度制御装置を備えたクリーンルーム内の標準的排気内）で実行できる。このデポジションおよびスピニング中、およびこれら工程の後では、膜１４からエタノールおよび水が蒸発するが、グリセロールの揮発性は低いのでグリセロールの実質的な蒸発は生じない。このような蒸発は薄膜１４を収縮し、ゾルのシリカ成分を濃縮し、薄くされた薄膜１８を形成する。図１２Ｂは実質的にすべての（約９５％またはそれ以上の）水が除かれた後に得られる薄くされたゾル膜１８を示している。このような膜の濃縮により、一般に数分内でゲル化が生じる。

【００８９】第３実施例に記載のプロセスの後に、一般に次のような処理が続く。ゲル化後、薄膜の湿潤ゲル１８は多孔質の固体および孔内流体を含み、１つ以上の制御された温度で時間をかけてエージングすることが好ましい。過臨界流体抽出を含むいくつかの方法のうちの１つにより、実質的に密度を高めることなくエージングされた膜１８を乾燥できる。しかしながら第３実施例に記載のように、エージング流体から膜１８を空気乾燥することが好ましい。このナノ多孔質誘電体は次に第１実施例に記載のように、乾燥のベーキングおよび／または表面改質処理を行うことができる。この実施例の（表面改質前の）理論的誘電率は２．５である。

【００９０】多孔率と誘電率を別の値とするように、他の溶剤対反応体の比を使用できる。図１４はデポジットされたゾルからすべてのエタノールが蒸発する場合の金属原子に対するグリセロール分子のモル比とナノ多孔質誘電体の多孔率との理論的な関係を示す。一般により高い多孔率のグリセロールゲル（一般に約０．５１ｇ／ｃｃよりも低い）は、溶剤交換または乾燥中に収縮を減少させる他の方法を必要とする。他方、より低い多孔率のゲルは早期のゲル化を防止するような注意を必要とする。このような方法はｐＨ調節、温度管理またはその他当業者に知られている方法から構成できる。ある応用例では、ゲル化後に高揮発性溶剤の蒸発を可能にするように認めることも可能である。

【００９１】上記のように、溶剤交換を行わなくても、より高い密度のグリセロール基ゲル（一般に約０．６４ｇ／ｃｃより大）をエージングし、ほとんど収縮することなく乾燥できる。エージングしていないウェーハを小容積の炉または小さい容器に入れ、この容器をホットプレート上に載せることができる。オプションの蒸発の後に容器を常温でシールする。この容器は温度をランプ関数に従って上昇させ、膜を迅速にエージングし、エージング／乾燥流体の粘性を下げる時は容器はシールされた状態のままである。（温度上昇中に可能な）十分なエージングを行った後は、ゲルは乾燥の準備が完了している。グリセロールの沸点近くの温度では、グリセロールの粘性は（所定の多孔率のエージングされた膜の強度と比較して）十分小さくできるので炉の雰囲気内のグリセロールを除去し、膜を直接乾燥できる。ここで、最も要求の多い低密度の応用例では、乾燥空気をグリセロールの沸点よりも上に上げることにより、多少低い表面張力を得ることができる。これらのケースでは炉は圧力に耐えなければならない（１～３のＭＰａの温度でほとんどの準臨界的乾燥状態を処理できる）。更に、炉内の雰囲気内のグリセロールを特に最初はゆっくりと除くように注意を払う必要がある。炉内のグリセロールは例えば真空ポンプにより圧力をブリードするか、またはガスを用いてグリセロールをスイープすることによって除去できる。グリセロールを除く間に炉の温度を一定に保持するか、または上昇し続けてよい（ガスでグリセロールをスイープする間は炉をベーキング温度までランプ状に上昇してもよい）。膜からの蒸発を最小にするよう、加熱中にいくらかのグリセロールを導入できるが、加熱中にグリセロールを導入しなくても蒸発によって膜厚が薄くならないように、炉の容積を十分小さくすることが好ましい。恐らく一時的な収縮も解消するように、膜が過臨界的乾燥を必要とする場合、当業者に周知のようにＣＯ$_2$による溶剤交換を利用することが好ましい。

【0092】バルクアエロゲルに対し薄膜アエロゲルと同じ原液を使用できるが、処理方法は実質的に異なっている。異なった原液混合物を用いる場合、バルクゲルに異なる多孔率を与えるのに次の例を適用できる。本発明のバルクアエロゲルの実施例によれば、２０８．０ｍｌのテトラエトキシシラン（ＴＥＯＳ）と、６１．０ｍｌのグリセロールと、３．５６ｍｌのエタノールと、１６．８ｍｌの水と、０．６７ｍｌの１ＭのHNO_3とを混合し、～６０℃で１．５時間還流し、原液を形成する。これと等価的な表現をすれば、０．９３モルのＴＥＯＳと、０．８４モルのグリセロールと、３．５６モルのエタノールと、０．９３モルの水と、６．８０Ｅの４モルのHNO_3を混合し、～６０℃で１．５時間還流する。これを強く混合し、一般に～７℃で冷蔵庫に保管し、使用するまで安定性を維持する。この原液はモールドに入れる前に常温に温めることが好ましい。モールドに注入後、エタノール、水および酸を放置して蒸発させるが、グリセロールの揮発性は低いので、グリセロールの実質的な蒸発は生じない。このような蒸発は原液の前駆物質ゾルの容積を減少し、ゾルのシリカ成分を濃縮する。モールドを満たす前に蒸発の少なくとも一部を生じさせることが認められる。この充填前の蒸発は、モールドの形状充填後の実質的な蒸発に適していない場合、例えばモールドの露出した表面積が少ない場合、またはモールドの形状が収縮に合致していない場合には特に有効である。このような蒸発は不要であるが、触媒を用いなくてもゲル化が早くなったり、ゲル化後の収縮が少ないといういくつかの利点がある。

【0093】この蒸発後、ゾルはゲル点で孔内流体に対するシリコンの概略的に知られた値を有する。この比は（残留する水、継続する反応および付随的な蒸発による変化がわずかな）前駆物質混合物内のグリセロールに対するＴＥＯＳの比にほぼ等しい。この方法はゲルが永久的に崩壊するのをかなり防止するので、この比は製造されるアエロゲルの密度を決定する。蒸発中にゾルがゲル化しない場合、このゾルは水、エタノールおよび酸のほぼすべてが蒸発した後すぐにゲル化する。

【0094】これとは異なり、モールドに充填する前に０．５Ｍの硝酸アンモニウムで前駆物質に触媒作用させてもよい。この混合物を用いるとゾルは一般に数分内でゲル化する。モールドから湿潤ゲルを除きエタノールおよび水を蒸発させる。

【0095】一般に、ゲルはこの蒸発中に収縮する。しかしながら、他の方法を用いた場合と同じように、蒸発が実質的に完了するとゾルはゲル点で孔内流体に対するシリコンのほぼ知られている比を有する。この比は（残留水、継続する反応および付随的蒸発に起因するわずかに変化した）前駆物質混合物中のグリセロールに対するＴＥＯＳの比にほぼ等しい。この方法は、ゲルが永久的に崩壊することをかなり防止するので、この比は製造されるアエロゲルの密度を決定する。

【0096】ゲル化後、湿潤ゲルは多孔性固体と孔内流体を含み、１つ以上の制御された温度で時間をかけてエージングさせることが好ましい。このエージングは基板およびゲルを約２４時間の間、約２５℃に維持するか、またはこれらを密閉容器内で約５分間１３０～１５０℃に加熱することにより完了することが好ましい。これらの高温エージングパラメータは５ｍｍ径のバルクアエロゲルに対して有効である。しかしながら、湿潤ゲルの低熱伝導度により高温で加速されるエージング時間と温度の組み合わせはバルクゲルの形状に大きく依存する。

【0097】この初期のエージング後にモールドからゲルを除き、母液（すなわちエージングまたは乾燥のために溶剤交換を行わない場合のエージング終了時に残留している孔内流体）から直接乾燥する。約５００℃までゆっくりとランプ状に上昇させ、この温度に保持すると、ゲルが乾燥される。

【0098】母液から直接乾燥する代わりに、特に高多孔率ゲルの場合、溶剤交換法を実行することが好ましい。この溶剤交換法は１工程または２工程プロセスで実行できる。この第１の工程でエージング流体を中間流体と置換し、第２工程で中間流体を低表面張力乾燥流体、例えばヘプタンで置換することが好ましい。この方法では、モールドからゲルを除き、このゲルをエタノールを含む密閉チューブ内に入れ、８時間の間、５０℃で孔内流体を交換することが好ましい。８時間の期間終了後にゲルをエタノールでリンスし、これを５０℃のオーブン内の新しいエタノール内に保管する。３～６時間後に同様にしてエタノールをヘキサンに置換する。この溶剤交換方法により、我々は乾燥前にグリセロールを含む流体のすべてを除くことができる。この乾燥流体（この場合ヘプタン）を最終的に放置して湿潤ゲルから蒸発させ、乾燥アエロゲルを形成する。エージング流体に可溶性の液体から膜を満足できる状態に乾燥できれば中間流体は不要である。多くの場合、エタノールまたはその他の適当な溶剤から湿潤ゲルを乾燥できる。

【0099】乾燥後、アエロゲル上またはアエロゲル内にある残留物質、例えば有機物の除去を助けるため、短期間の間（例えば３００℃では１５～６０分間）アエロゲルをベーキングすることが好ましいことが多い。ある応用例では、乾燥ゲルをデヒドロキシル化（アニール）することも望ましい。これは表面改質剤、例えばトリメチルクロロシラン（ＴＭＣＳ）、ヘキサメチルジシラザン（ＨＭＤＳ）またはヘキサフェニルジシラザン蒸気を含む乾燥雰囲気内に乾燥アエロゲルを入れることによって実行できる。ＨＭＤＳは乾燥されたゲルの孔の表面に結合した多量の水および／またはヒドロキシル基をメチル基に置換させる。この置換は常温またはそれよりも高い温度で実行できる。この置換は水および／またはヒドロキシル基を除くことができるだけでなく、乾燥ゲルを

疎水性（水反撥性）にもする。ヘキサフェーニルジシラザンも水および／またはヒドロキシル基を除き、乾燥ゲルを疎水性にする。しかしながらフェニル基はメチル基よりも温度安定性が高い。

【０１００】本発明のエチレングリコールに基づく実施例によれば、モル比で１：２．４：１．５：１：０．０４２でテトラエトキシシラン（ＴＥＯＳ）、エチレングリコール、エタノール、水および酸（１ＭのHNO_3）を混合し、～６０℃で１．５時間還流する。この混合液を冷却した後、溶液をエタノールで希釈し、７０容積％の元の原液と３０容積％のエタノールの組成とする。これを激しく混合し、一に～７℃で冷蔵庫に保管し、使用するまで安定性を維持する。膜デポジション前に溶液を室温に温める。原液を０．２５ＭのNH_4OH触媒の混合物（１０：１の容積比）を組み合わせて混合する。常温で基板１０に３～５ｍＬのこの前駆物質ゾルを分配し、基板を約５～１０秒の間、（所望の膜厚に応じて）１５００～５０００ｒｐｍでスピニングし、ゾルの薄膜１４を形成する。制御されていない雰囲気内でこのデポジションを行うことができる。しかしながら、標準的な湿度制御装置を備えたクリーンルームでゾルをデポジットし、ゲル化することが好ましい。このデポジションおよびスピニング中、更にその後に膜１４からエタノールと水の混合物が蒸発するが、エチレングリコールの揮発性は低いので、エチレングリコールの実質的な蒸発は生じない。この蒸発は薄膜１４を収縮し、ゾルのシリカ成分を濃縮し、厚みを薄くされた膜１８を形成する。図１２Ｂはエタノールのほぼすべて（約９５％またはそれ以上）が除かれた後に得られる厚みを薄くされたゾル膜１８を示す。触媒と組み合わされたこの濃縮により一般に数分または数秒内でゲル化が生じる。

【０１０１】膜１８はゲル点で孔内流体に対するシリコンの概略的に知られた比を有する。この比は（残留水、継続する反応および付随する蒸発により変化がわずかな）デポジットされた当初のゾル内のエチレングリコールに対するＴＥＯＳの比にほぼ等しい。この比はゲルの崩壊が防止される程度にゾルの薄膜から製造されるアエロゲル膜の密度を決定する。

【０１０２】ゲル化後、薄膜の湿潤ゲル１８は多孔性固体と孔内流体を含み、１つ以上の制御された温度で時間をかけて、例えば常温で約１日かけてエージングさせることが好ましい。孔内流体は処理中に多少変化することに留意すべきである。これら変化は継続する反応および／または蒸発／凝縮に起因するものである。エージングは約１００℃で約５分の間デバイスを低容積エージングチャンバー内に入れることにより実行することが好ましい。

【０１０３】過臨界的流体抽出または溶液交換後空気乾燥を行う方法を含む種々の方法のうちの１つにより、実質的な高密度化を行うことなく、エージングされた膜１８を乾燥できる。しかしながら、第３のグリセロールを用いた実施例に記載されているようにエージング流体から膜１８を空気乾燥することが好ましい。次に、第１のグリセロールを用いた実施例に記載されているように、ナノ多孔質誘電体に乾燥後のベーキングおよび／または表面改質工程を施すことができる。

【０１０４】本発明の別のエチレングリコールに基づく実施例によれば、モル比で１：４：１：０．０４２でテトラエトキシシラン（ＴＥＯＳ）、エチレングリコール、水および酸（１ＭのHNO_3）を混合し、～６０℃で１．５時間還流する。これを一般に～７℃で冷蔵庫に保管し、使用するまで安定性を維持する。この溶液は膜デポジション前に室温に温めることが好ましい。常温で基板１０に３～５ｍＬのこの前駆物質ゾルを（触媒を用いることなく）分配し、基板を約５～１０秒の間、（所望の膜厚に応じて）１５００～５０００ｒｐｍでスピニングし、ゾルの薄膜１４を形成する。制御されていない雰囲気内でこのデポジションを行うことができる。しかしながら、標準的な湿度制御装置を備えたクリーンルームでゾルをデポジットし、ゲル化することが好ましい。このデポジションおよびスピニング中、更にその後に膜１４からエタノールおよび水が蒸発するが、エチレングリコールの揮発性は低いので、エチレングリコールの実質的な蒸発は生じない。この蒸発は薄膜１４を収縮し、ゾルのシリカ成分を濃縮し、厚みを薄くされた膜１８を形成する。図１２Ｂはエタノールのほぼすべて（約９５％またはそれ以上）が除かれた後に得られる厚みを薄くされたゾル膜１８を示す。この濃縮により一般に数分内でゲル化が生じる。

【０１０５】ゲル化後、薄膜の湿潤ゲル１８は多孔性固体と孔内流体を含み、１つ以上の制御された温度で時間をかけて、例えば常温で約１日かけてエージングさせることが好ましい。孔内流体は処理中に多少変化することに留意すべきである。エージングは約１００℃で約５分の間デバイスを低容積エージングチャンバー内に入れることにより実行することが好ましい。

【０１０６】過臨界的流体抽出または溶液交換後空気乾燥を行う方法を含む種々の方法のうちの１つにより、実質的な高密度化を行うことなく、エージングされた膜１８を乾燥できる。しかしながら、第３のグリセロールを用いた実施例に記載されているようにエージング流体から膜１８を空気乾燥することが好ましい。次に、第１のグリセロールを用いた実施例に記載されているように、ナノ多孔質誘電体に乾燥後のベーキングおよび／または表面改質工程を施すことができる。

【０１０７】この点までの説明は、密閉容器内のエージングの利点のいくつかを示すものである。適当なエージング用チャンバーは存在していないようなので、このプロセスを実現するために我々が発明したチャンバーについて説明することとする。図１６Ａ、１６Ｂ、１６Ｃに

エージング用容器の一実施例が示されている。この実施例では処理装置がほぼ平面状のプレート２２を有する本体２０を含み、このプレートに弾性シール２４が取り付けられている。プレート２２は作動中、薄膜に間隙を提供するのに必要な程度平面状であればよく、基礎となるプロセス（例えば半導体製造法）に適合する任意の材料で製造できるが、熱伝導率の高い材料、例えばステンレススチール、ガラスまたはアルミが好ましい。弾性シール２４は湿潤ゲル処理温度および孔内流体に耐えるように設計することが好ましく、当業者にはテフロン基およびネオプレン基材料を含む適当な材料が多く知られている。装置内で使用される温度制御の性質に応じてシール２４をほぼ実質的に断熱性とするか、または熱伝導性とするかの決定するのが好ましい。

【０１０８】作動中、本体２０は図１６Ｃに示すように基板２６に載せるだけでよい。この基板は光学的な基板、例えばガラスまたはプラスチック、またはＳｉウェーハのような半導体基板でよい。この実施例ではシール２４は大気圧シールとして、更に基板表面２８と、チャンバー表面３０と、シール２４によって形成されるチャンバー３２の容積を設定するスペーサの双方として機能する。例えばシール２４はプレート２２の重量により約１ｍｍの厚さに圧縮され、よって基板２６に本体２０を載せた時、１ｍｍ高のチャンバー３２を形成するように設計できる。多くの薄膜用では、基板２６を処理する際のわずかな程度の蒸気のリークは最終的な膜の性質に大きな影響を与えるわけではないので、チャンバー３２は実質的にシールするだけでよい。

【０１０９】本体２０はアエロゲル薄膜プロセス中の多くの点で利用できる。この本体２０は湿潤ゲル薄膜に対するエージング用チャンバーとして、かかる膜のための保管または運搬用チャンバーとして、または乾燥チャンバーとして、ゾル膜がゲル化する前の蒸発を制限するのに使用できる。これら応用例のいずれにおいてもゾルおよびゲルの薄膜の双方は、極端に少量の液体しか含んでいないので、膜からの実質的な蒸発を防止するのに、限られた容積のチャンバーでよいと認識される。

【０１１０】別の実施例では本体２０は図１７Ａおよび１７Ｂに示されるように、更に多くの機素を含むことができる。この実施例では本体２０は更に基板ホルダ３６と基板温度制御手段３４とを含む。この実施例は基板の外に位置するシール２４（またはあるケースではシール２４を省略することもできる）の別の特徴を示しており、薄膜を基板表面２４の全体に形成できるようになっている。チャンバー３２を閉じると平面状プレート２２とウェーハホルダ３２が熱結合し、よって熱制御手段３４を使用して本体２０、基板２６およびチャンバー３２の温度を同時に制御できる。

【０１１１】図１８Ａおよび１８Ｂに示される別の実施例ではシール２４は平面上プレート２２とウェーハホルダ３６とをある程度熱絶縁している。これにより温度制御手段３４は基板の温度を制御できるが、一方、平面状プレートの温度を制御するのに別個の温度制御手段３８が使用されている。かかる手段は平面状プレート２２の温度を選択的に下げてチャンバー表面３０上での凝縮を促進できるので、湿潤ゲル膜を乾燥できるという利点を有する。

【０１１２】図１９Ａ、１９Ｂ、１９Ｃは、これらエージング用チャンバーの別の特徴を示している。例えば図１９Ａでは基板２６は倒立した位置で処理される状態が示されている。この実施例ではチャンバー表面３０上の偶発的な、または意図的な凝縮物が基板表面２６上に落下しないようにこれを集めることができるようになっている。図１９Ｂでは基板２６は倒立された状態で処理されているだけでなく、第１溶剤の層４２（少なくとも１つの孔内流体と同じ組成から成ることが好ましい）がチャンバーを閉じる前に第１溶剤供給チューブ４０からチャンバー表面３０へ分配されている。この実施例では層４２を使用して処理雰囲気の飽和を助けることができるので、この結果、基板２６からの孔内流体の蒸発が少なくなっている。

【０１１３】図１９Ｃでは少なくとも１つのポート４６（このポートは閉じることができる）を介してチャンバー３２に、ある雰囲気調節手段４４が接続されている実施例が示されている。雰囲気調節手段４４は真空を発生させたり、適当にチャンバー３２を過剰圧力としたり、チャンバー３２内の雰囲気を交換したり、孔内流体の蒸気をチャンバー３２に供給するように使用できる。この実施例は、例えばチャンバー３２を大気圧力よりも高い圧力で作動することにより孔内流体の沸点よりも高い温度で薄膜をエージングするのに使用できる。この実施例はエージング後にチャンバー３２から孔内流体の蒸気の少なくとも一部を除き、よって薄膜を乾燥できるようにするのにも使用できる。

【０１１４】数種類の実施例により、以上で本発明について説明したが、本発明の範囲内でこれら工程の多くを変更できるし、全体のプロセスを高めるのに他の工程を加えることもできる。例えばスピンコーティングの代わりに他の一般的な方法、例えば浸漬コーティング、フローコーティングまたはスプレーコーティングにより初期の薄膜をデポジットしてもよい。同様に溶剤交換方法ではスピンコーティングの代わりに浸漬コーティング、スプレーコーティングまたは液体もしくは蒸気状の溶剤内に浸漬する方法を使用できる。蒸気状の溶剤を使用する場合、雰囲気よりも低い温度にウェーハを冷却し、よってウェーハ上での凝縮を促進してもよい。上記方法を用いない場合、かかるプロセスでは水は溶剤と見なされるが、このような応用例での説明上、水は溶剤とは見なさない。

【０１１５】グリセロールおよびエチレングリコールの

双方は、それぞれユニークな利点を有するが、低収縮率のナノ多孔質の誘電体を製造するのに利用できるその他の低揮発性溶剤がある。溶剤を分析して予想される蒸発レートを決定することが好ましいが、低揮発性予想の選択を先に優先できる。常温で低い蒸発レートを有するほとんどすべての溶剤は１４０℃よりも高い沸点を有する。１４０℃よりも低い沸点を有するある溶剤を利用できるが、１６０℃よりも高い沸点、より好ましくは１９０℃よりも高い沸点を有する溶剤の蒸発レートが一般に好ましいことが理解できよう。２０３℃よりも高い沸点を有する溶剤も、４０～８０℃で短時間の間で、ほとんど雰囲気制御することなくデポジションおよび／またはエージングに適した十分低い蒸発レートを有する。ほとんど雰囲気制御しない状態で１００～１５０℃で処理するには、２７０℃よりも高い沸点を有する溶剤を使用することが好ましい。これにより、好ましい沸点の下限が大まかに優先される。また、好ましい沸点の上限に対する大まかな優先もある。沸点が５００℃よりも高いほとんどの溶剤は粘性となるので、これらは処理中に更に注意が必要である。一般に、より有効な溶剤は３６０℃よりも低い沸点、好ましくは３００℃よりも低い沸点を有する。デポジション中にゾルを希釈したり、または加熱することが好ましくない場合、２００℃よりも低い沸点を有する低揮発性よりもを使用することが好ましいこともある。望ましい性質のすべてを与えるような溶剤が全くない場合、性能を改善するのに２つ以上の溶剤を混合してもよい。従って、低揮発性溶剤の選択に関する我々の初期のこれまでの優先的な判断基準は、１７０～２５０℃の範囲内にある沸点があること、および（ＴＥＯＳゲルに対しては）溶剤が水およびエタノールの双方と混和できることであった。これらのこれまでの優先判断基準に基づき、グリセロールおよびエチレングリコール以外の適当な低揮発性溶剤として１，４－ブチレングリコールと１，５－ペンタンジオールが候補として挙げられた。

【０１１６】常温よりも高い温度でデポジションおよびエージングを行うことが好ましい場合、このことは更に別の可能性を与える。１つの改善とは常温では液体でなく固体であるような溶剤を使用することである。これにより更に多くの材料を潜在的に使用できることとなる。より高い融点のこれら材料の多くは常温で液状の溶剤（液状溶剤）が高温の蒸着およびエージング温度で有している低揮発性よりもより低い揮発性を有している。融点の上限温度は不要であるが、プロセスを簡略化するにはこれらの常温で固体の溶剤（固体溶剤）は６０℃よりも低い融点、好ましくは４０℃よりも低い融点を有していなければならない。潜在的な固体溶剤に対する望ましい特徴とは、この溶剤がアモルファス相となるように容易に凝固することが挙げられる。このようなアモルファス凝固により偶発的な冷却中にゲルが損傷する機会が少なくなる。更に、この性質によりフリーズドライすれば溶剤を除くことが可能となる。前駆物質の温度を固体溶剤の融点よりも高く維持する別の方法は、固体溶剤をキャリア液内に溶解することである。このキャリア液は水、アルコールまたは薄膜アエロゲル／キセロゲルの処理に一般に使用される他の任意の液体でよい。このキャリア液体はキャリアとしてのみ導入される適合性のある液体でもよい。

【０１１７】グリセロールおよびエチレングリコールの驚くべき良好な性質は、他の好ましい溶剤への手掛かりを与える。我々はエチレングリコールまたはグリセロールとも若干異なる性質を与え、更にそれらの利点の多くも維持するいくつかの溶剤を識別した。最も将来性に優れた別の溶剤としては、１，２，４－ブタントリオール；１．２，３－ブタントリオール；および２－メチルプロパントリオール；および２－（ヒドロキシメチル）－１，３－プロパンジオール；１－４，１－４，ブタンジオール；および２－メチル－１，３－プロパンジオールがある。その他の潜在的な溶剤としてはポリオール単独か、またはポリオールとエチレングリコール、またはその他の溶剤との組み合わせがある。

【０１１８】低揮発性溶剤をこのように使用することにより、デポジション、ゲル化および／またはエージング中の必要な雰囲気制御をゆるやかにできる。この理由は、飽和は好ましくは回避すべきであるが、雰囲気の溶剤濃度は過剰な蒸発を行わなくても低下できるからである。このような広い濃度の幅を使用してデポジションチャンバー全体で（特にウェーハおよび蒸発性冷却効果の近くで）より広い温度変動を可能にできる。初期の目標は少なくとも１℃の温度変動を可能にすることである。従って、雰囲気内の低揮発性溶剤の蒸気濃度は溶剤蒸気の凝縮温度（露天に類似する）が基板の温度よりも少なくとも１℃低くなるようにすべきである。実際には重大なことは、デポジットされたゾルおよび／またはゲル状ゾルの表面である。しかしながら、ゾルの薄膜の性質はゾルと基板との温度差を少なく維持する。基板温度を測定することのほうがより簡単であるので、本特許ではこれら２つの温度を相互に交換可能に使用する。ある条件下では１℃の温度の均一性を得ることができるが、容積発生は恐らく少なくとも３℃の許容幅、好ましくは１０℃の許容幅を必要とする。しかしながら最終目標は制御されていないか、実質的に制御されていない雰囲気内でデポジットし、ゲル化し、エージングすることにある。この最も好ましい方法（実質的に制御されていない雰囲気）では、デポジット、ゲル化およびエージング中の雰囲気制御は標準的なクリーンルーム温度および湿度制御に限定されるが、ウェーハおよび／または前駆物質ゾルは独立した温度制御装置を有することができる。このような実質的に制御されていない雰囲気が過剰な蒸発を可能にする場合、受動的またはわずかであることが好まし

い能動的雰囲気制御が必要となり得る。このような応用例では、比較的小さい容器内にウェーハを置くことに自動制御が限定される。この容器は一部または完全にシールでき、溶剤の液体リザーバを含んでもよいし、また含まなくてもよい。しかしながら、この容器はウェーハ、容器の雰囲気および／またはリザーバのための外部環境制御装置は有しない。

【０１１９】基本方法の変更例の別の例としては、乾燥前に（更に一般に必ずしもというわけではないがエージング後に）、薄膜湿潤ゲル１８は表面改質剤で改質された孔表面を有することができる。この表面改質工程は孔の壁上のかなりの数の分子を別の種の分子と置換する。表面改質剤を塗布する場合、一般に表面改質剤を加える前に湿潤ゲル１８から水を除くことが好ましい。純粋なエタノール内でウェーハをリンスし、好ましくは第１実施例における溶剤交換法に記載されているように、低速度のスピンコーティングにより水を除くことができる。水は表面改質剤、例えばＨＭＤＳと反応するので、このように水を除去すると有利である。しかしながら、このことは必要ではない。我々のグリセロールを用いた新しい方法では、孔の崩壊の防止を助けるための表面改質は実施する必要はないが、この表面改質を使って乾燥ゲルに他の望ましい性質を与えることができる。潜在的に好ましい性質の例としては、疎水性、小さい誘電率、所定の化学薬品への提供力が大きいこと、および温度安定性が改善されていることが挙げられる。望ましい性質を与えることができる潜在的な表面改質剤としてはヘキサメチルジシラザン（ＨＭＤＳ）、アルキルクロロシラン（トリメチルクロロシラン（ＴＭＣＳ）、ジメチルクロロシラン等）、アルキルアルコキシシラン（トリメチルメトキシシラン、ジメチルジメトキシシラン等）、フェニル化合物およびフルオロカーボン化合物が挙げられる。１つの有効なフェニル化合物としてヘキサフェニルジシラザンがある。その他の有効なフェニル化合物は一般に基本化学式$Ph_xA_ySiB_{(4-x-y)}$に従い、ここでＰｈはフェニル基であり、ＡはＣｌまたはＯＣＨのような反応基であり、Ｂはリガンドであり、このリガンドは２つある場合、同一または異なる基でもよい。これらフェニル表面改質剤の例としては、１個のフェノール基を備えた化合物、例えばフェニルトリクロロシラン、フェニルトリフルオロシラン、フェニルトリメトキシシラン、フェニルトリエトキシシラン、フェニルメチルクロロシラン、フェニルエチルジクロロシラン、フェニルジメチルエトキシシラン、フェニルジメチルクロロシラン、フェニルジクロロシラン、フェニル（３－クロロプロピル）ジクロロシラン、フェニルメチルビニルクロロシラン、フェニルエチルジメチルクロロシラン、フェニルトリクロロシラン、フェニルトリメトキシシラン、フェニルトリ（トリメチルシロキシ）シラン、およびフェニルアリルジクロロシランが挙げられる。これらフェニル表面改質剤の他の例としては、２個のフェノール基を有する化合物、例えばジフェニルジクロロシラン、ジフェニルクロロシラン、ジフェニルフルオロシラン、ジフェニルメチルクロロシラン、ジフェニルエチルクロロシラン、ジフェニルジメトキシシラン、ジフェニルメトキシシラン、ジフェニルエトキシシラン、ジフェニルメチルメトキシシラン、ジフェニルメチルエトキシシランおよびジフェニルジエトキシシランがある。これらフェニル表面改質剤には更に３個のフェノール基を有する化合物、例えばトリフェニルクロロシラン、トリフェニルフルオロシランおよびトリフェニルエトキシシランも含まれる。他の重要なフェニル化合物、すなわち１，３－ジフェニルテトラメチルジシラザンはこの基本化学式の例外である。これらリストは完全に網羅したものではないが、基の基本的な性質を伝えている。有効なフルオロカーボン基表面改質剤には、（３，３，３－トリフルオロプロピル）トリメトキシシラン、（トリデカフルオロ－１，１，２，２－テトラヒドロオクチル）－１－ジメチルクロロシランおよびヒドロキシル基と共有結合を形成する反応基、例えばＣｌまたはOCH_3を有する他のフルオロカーボン基が含まれる。

【０１２０】上記パラグラフは従来の用途のための代表的な有効な性質のいくつかをリストアップしたものである。しかしながら、異なる望ましい性質を有することがあるナノ多孔質誘電体およびアエロゲルの潜在的な用途は他にもある。このような他の潜在的に望ましい例としては、疎水性、電気伝導度が高いこと、絶縁破壊電圧が高いこと、所定の化学薬品との反応性が高かったり低かったりすること、および揮発性が高いことが挙げられる。このリストは完全に網羅したものではない。しかしながら用途に応じて種々の多数のタイプの性質が望ましいことが分かっている。従って、ヒドロキシル基と共有結合を形成するその他多くの材料は、他の潜在的に好ましい性質を与え得る潜在的な表面改質剤となることが明らかである。

【０１２１】本発明はゲル化触媒、例えば水酸化アンモニウムを使用することも含む。更に本発明は、水酸化アンモニウムの代わりに他のゲル化触媒を使用することを認め、および／またはデポジション後にゲル化触媒を添加することも認めるものである。一般に、これら別の触媒はゾルのｐＨを変える。ｐＨを上げる触媒を使用することが好ましいが、酸の触媒を使用できる。一般に酸触媒により処理時間が長くなり、塩基で触媒作用されたプロセスよりも誘電体の密度は高くなる。その他の好ましいゲル化触媒の例としてアンモニア、揮発性アミン種（低分子量アミン類）および揮発性フッ素種が挙げられる。デポジション後に触媒を添加する時は、この触媒は蒸気、ミストまたは他の蒸気として添加することが好ましい。

【０１２２】本発明は別個の表面改質工程を実行するこ

となく常温および大気圧でのナノ多孔質誘電体を製造可能にするものである。この新規な方法は実質的な高密度化を防止することが求められているわけではないが、乾燥前に過臨界的乾燥すなわち表面改質工程を使用することを排除するものではない。この方法は大きな（例えば５０ｎｍ）の決勝を防止するようフリーズ速度が十分高速となる程度にフリーズドライ方法とも適合している。一般にこの新規な方法は、従来のほとんどのエーロゲル技術と適合性がある。

【０１２３】他の例の改質方法は反応雰囲気および／または温度に関連している。同じチャンバーまたは同じ雰囲気内でコーティングおよびゲル化を実行する必要はない。例えば基板の温度はゲル化を遅らせるように下げるか、または表面改質および／またはゲル化の速度を速くするように高温とすることができる。更に、蒸発レートおよび／またはゲル化時間を制御するように全体の圧力および／または温度を変えてもよい。一般に４０℃以上の高温処理が実行されるが、５０℃が好ましく、７０℃が更に好ましい。高温で作動させる時には溶剤の沸騰を防止するように注意を払う必要がある（例えば反応雰囲気内の部分圧は十分高くしなければならない）。

【０１２４】反応体の代表的な例としてこれまでＴＥＯＳが使用されてきたが、その他の金属アルコキシドを単独またはＴＥＯＳと組み合わせて、または相互に使用し、シリカネットワークを形成できる。これら金属アルコキシドとしては、テトラメトキシシラン（ＴＭＯＳ）、メチルトリエトキシシラン（ＭＴＥＯＳ）、１，２－ビス（トリメトキシシリル）エタン（ＢＴＭＳＥ）、これらの組み合わせおよび当業者に知られているその他のシリコン基金属アルコキシドが挙げられる。ゾルは当業者に知られている他の金属、例えばアルミニウムおよびチタンのアルコキシドからゾルを形成吸いることも可能である。当業者に知られているその他の前駆物質ゾルとしては粒状金属酸化物および有機前駆物質が挙げられる。２つの代表的な粒状金属酸化物としては発熱（発煙）シリカおよびコロイド状シリカがある。代表的な有機前駆物質としてメラミン、フェノールフルフラールおよびレソルシノールがある。代替反応体の他に代替溶剤を使用することもできる。エタノールの好ましい代替物の例はメタノールおよびその他の高級アルコールがある。称賛の代わりに前駆物質ゾル安定剤として他の酸を使用することもできる。

【０１２５】別の変更例は前駆物質ゾル内の適度な大きさ（１分子当たり１５～１５０個のモノマー）のオリゴマーの形成を可能にし、および／または促進できるようにすることである。これら、より大きなオリゴマーはデポジットされたゾル内のゲル化プロセスをスピードアップできる。大きなオリゴマーを含むゾルは小さいオリゴマーを含むゾルよりも粘性が大きくなり得る。しかしながら粘性が安定である限りこのような高い粘性は当業者に周知の方法、例えば溶剤の比率およびスピン条件を調節することにより保証できる。このような望ましい安定な粘性を得るのを助けるためにデポジット前にオリゴマー化を低速にしたり、実質的に停止させる必要がある。オリゴマー化を促進する可能性のある方法としては、前駆物質ゾルを加熱し、溶剤を蒸発させ、または少量のゲル化触媒、例えば水酸化アンモニウムを加えることが挙げられる。オリゴマー化を抑制する可能性のある方法としては、前駆物質ゾルを冷却すること、ゾルを溶剤で希釈すること、前駆物質ゾルを凝縮およびゲル化を最小とするｐＨに回復させること（上記例示した水酸化アンモニウムと組み合わせて硝酸を使用できる）が挙げられる。

【０１２６】以上で数種の実施例により本発明を説明したが、当業者には種々の変形および変更を思いつくことができよう。本発明は特許請求の範囲内にあるかかる変形および変更例を含むものである。

【０１２７】本願の優先権主張の基礎となった米国仮特許出願は次のとおりである。

出願日	出願番号	代理人整理番号	発明の名称
1995.11.16	60/006,852	TI-21620P	エーロゲル薄膜のための高速エージング技術

1996. 1. 24	60/010,511	TI-21622P	ナノ多孔質誘電体薄膜表面改質
1995. 11. 16	60/006,853	TI-21623P	マルチ溶剤系からのアエロゲル薄膜の形成
1995. 11. 16	60/006,861	TI-21624P	デポジション後の触媒を使ったナノ多孔質誘電体の形成
1996. 3. 4	60/012,764	TI-22177P	薄膜ナノ多孔質誘電体を形成するためのグルコールを使用する方法
1996. 3. 4	60/012,765	TI-22778P	エーロゲルのためのグルコール基前駆物質
1996. 3. 4	60/012,763	TI-22179P	受動的基板上に薄膜アエロゲルを形成するためのグルコールを使用する方法
1996. 3. 4	60/012,799	TI-22780P	バルクアエロゲルを形成するためのグリコールを使った方法
1996. 3. 25	60/014,009	TI-22781P	アエロゲルのためのポリオール基前駆物質
1996. 3. 25	60/014,005	TI-22782P	半導体基板上に薄膜アエロゲルを形成するためのポリオールを使った方法
1996. 3. 25	60/014,008	TI-22783P	受動的基板上に薄膜アエロゲルを形成するためのポリオールを使った方法
1996. 3. 25	60/014,146	TI-22784P	バルクアエロゲルを形成するためのポリオールを使った方法
1996. 3. 4	60/012,800	TI-22788P	アエロゲルを形成するための低揮発性溶剤を使った方法
1996. 7. 31	60/022,842	TI-23260P	飽和多孔質膜を熱処理するためのデバイス

【０１２８】以上の説明に関し、更に以下の項を開示する。

（１）アエロゲル前駆物質反応体と、ポリオールを含む第１溶剤とを備え、前記反応体における金属原子に対する前記第１溶剤の分子のモル比が少なくとも１：１６である金属基ナノ多孔質アエロゲル前駆物質ゾル。

（２）金属アルコキシド、少なくとも一部が加水分解された金属アルコキシド、粒状金属酸化物およびそれらの組み合わせから成る群から選択されたアエロゲル前駆物質反応体と、ポリオールを含む第１溶剤とを備え、前記反応体における金属原子に対する前記第１溶剤の分子のモル比が少なくとも１：１６である金属基ナノ多孔質アエロゲル前駆物質ゾル。

【０１２９】（３）前記ポリオールがグリセロールである前記２項記載のエーロゲル前駆物質ゾル。

（４）前記反応体内の金属原子に対する前記第１溶剤の分子のモル比が１２：１以下である、前記第２項記載のアエロゲル前駆物質ゾル。

（５）前記反応体内の金属原子に対する前記第１溶剤の分子のモル比が１：２〜１２：１の間である、前記第２項記載のアエロゲル前駆物質ゾル。

（６）前記反応体内の金属原子に対する前記第１溶剤の分子のモル比が１：４〜４：１の間である、前記第２項記載のアエロゲル前駆物質ゾル。

（７）前記反応体内の金属原子に対する前記第１溶剤の分子のモル比が２．５：１〜１２：１の間である、前記第２項記載のアエロゲル前駆物質ゾル。

【０１３０】（８）前記反応体がテトラエトキシシラン、テトラメトキシシラン、メチルトリエトキシシラン、１，１－ビス（トリメトキシシリル）エタンおよびそれらの組み合わせから成る群から選択された金属アルコキシドである、前記第２項記載のエーロゲル前駆物質ゾル。

（９）前記反応体がテトラエトキシシランである、前記第２項記載のアエロゲル前駆物質ゾル。

（１０）前記テトラエトキシシランが少なくとも部分的に加水分解されている、前記第９項記載のアエロゲル前駆物質ゾル。

（１１）更に水を含む、前記第２項記載のアエロゲル前駆物質ゾル。
（１２）前記第１溶剤がエチレングリコールである、前記第２項記載のアエロゲル前駆物質ゾル。
（１３）第２溶剤を更に含む、前記第２項記載のエーロゲル前駆物質ゾル。
（１４）前記第２溶剤がアルコールである、前記第１３項記載のアエロゲル前駆物質ゾル。
（１５）前記第２溶剤がエタノールである、前記第１３項記載のアエロゲル前駆物質ゾル。
（１６）ｐＨ変更剤を更に含む、前記第２項記載のアエロゲル前駆物質ゾル。
（１７）酸を更に含む、前記第２項記載のアエロゲル前駆物質ゾル。
（１８）前記酸が硝酸である、前記第１７項記載のアエロゲル前駆物質ゾル。
（１９）前記ゾルのｐＨが３～５の間である、前記第２項記載のアエロゲル前駆物質ゾル。
【０１３１】（２０）ゲル化触媒を更に含む、前記第２項記載のアエロゲル前駆物質ゾル。
（２１）前記ゲル化触媒が水酸化アンモニウムである、前記第２０項記載のアエロゲル前駆物質ゾル。
（２２）前記ゾルのｐＨが７～９の間である、前記第２０項記載のエーロゲル前駆物質ゾル。
（２３）前記ゾルの粘性が１～１２センチポアズである、前記第２項記載のアエロゲル前駆物質ゾル。
（２４）前記ゾルの粘性が１～５センチポアズである、前記第２項記載の前駆物質ゾル。
（２５）前記反応体が発熱シリカ、コロイド状シリカおよびそれらの組み合わせから成る群から選択されたものである、前記第２項記載の前駆物質ゾル。
【０１３２】（２６）少なくとも一部が加水分解されたテトラエトキシシランおよびエチレングリコールを含むアエロゲル前駆物質ゾル。
（２７）テトラエトキシシランに対するエチレングリコールのモル比が１：１６～１２：１の間である、前記第２６項記載のアエロゲル前駆物質ゾル。
【０１３３】（２８）シリコン基アエロゲル前駆物質と、ポリオールを含む第１溶剤とを備え、前記反応体におけるシリコン原子に対する前記第１溶剤の分子のモル比が少なくとも１：１６であるシリコン基アエロゲル前駆物質ゾル。
（２９）前記反応体内のシリコン原子に対する前記第１溶剤の分子のモル比が１２：１以下である、前記第２８項記載のアエロゲル前駆物質ゾル。
【０１３４】（３０）少なくとも一部が加水分解されたテトラエトキシシランおよびグリセロールを含むアエロゲル前駆物質ゾル。
（３１）テトラエトキシシランに対するグリセロールのモル比が１：１６～１２：１の間である、前記第３０項記載のアエロゲル前駆物質ゾル。
（３２）テトラエトキシシランに対するグリセロールのモル比が１：４～４：１の間である、前記第３０項記載のアエロゲル前駆物質ゾル。
【０１３５】（３３）本明細書にはアエロゲル前駆物質ゾルが開示されている。このアエロゲル前駆物質ゾルは、金属基アエロゲル前駆物質反応体と、ポリオールを含む第１溶剤とを備え、反応体における金属原子に対する第１溶剤の分子のモル比が少なくとも１：１６となっている。好ましくは第１溶剤はグリセロールであり、好ましくはこのアエロゲル前駆物質反応体は、金属アルコキシド、少なくとも一部が加水分解された金属アルコキシド、粒状金属酸化物およびそれらの組み合わせから成る群から選択できる。一般に反応体における金属原子に対する第１溶剤の分子のモル比は１２：１以下であり、好ましくは反応体における金属原子に対する第１溶剤の分子のモル比は１：２～１２：１の間である。ある実施例では反応体における金属原子に対する第１溶剤の分子のモル比は２．５：１～１２：１の間である。ある実施例では第１溶剤はグリコールを含む。ある実施例では反応体は少なくとも一部を加水分解できるテトラエトキシシランである。ある実施例では第１ポリオールは１，２，４－ブタントリオール；１，２，３－ブタントリオール；２－メチルプロパントリオール；および２－（ヒドロキシメチル）－１，３，プロパンジオール；１－４，１－４，ブタンジオール；および２－メチル－１，３－プロパンジオール、およびそれらの組み合わせから成る群から選択されたものである。本発明は雰囲気制御を行うことなく多孔率が制御された薄膜のナノ多孔質アエロゲルをデポジットし、ゲル化し、エージングし、乾燥することを可能にするものである。別の特徴によれば、本発明は雰囲気を受動的に制御するだけで、例えばエージングチャンバーの容積を制限するだけで、多孔率が制御された薄膜のナノ多孔質アエロゲルをデポジットし、ゲル化し、高温で短時間にエージングし、乾燥できるようにするものである。

【図面の簡単な説明】

【図１】飽和比率および溶剤のタイプに対する蒸発レートの変化を示すグラフである。
【図２】温度および雰囲気の飽和比率に応じたグリセロールの蒸発レートを示すグラフである。
【図３】ナノ多孔質シリカ誘電体の場合の多孔率と、屈折率と、誘電率の間の理論的関係を示すグラフである。
【図４】塩基性触媒に応じたバルクエチレングリコール基ゲルの（溶剤の蒸発がない場合の）ゲル時間の変化を示すグラフである。
【図５】非グリコール基ゲルおよびエチレングリコール基ゲルの場合の密度に対する弾性率の変化を示すグラフである。
【図６】本発明に係わるバルクグリセロール基ナノ多孔

質誘電体の孔径の分布を示すグラフである。

【図7】温度および雰囲気飽和比率に応じたエチレングリコールの蒸発レートを示すグラフである。

【図8】温度に対する蒸気圧の変化を示すグラフである。

【図9】5mm厚の容器内で乾燥した場合の薄膜の収縮を示すグラフである。

【図10】1mm厚の容器内で乾燥した場合の薄膜の収縮を示すグラフである。

【図11】Aはエタノールおよびメタノールとグリセロールとの混合物のアルコール容積分に対する粘性変化を示すグラフである。Bはメタノールおよびエタノールとエチレングリコールとの混合物のアルコール容積分に対する粘性変化を示すグラフである。

【図12】本発明に係わる薄膜のデポジション中の、いくつかの点における半導体基板の横断面図である。

【図13】本発明に係わるナノ多孔質誘電体のデポジションプロセスのフローチャートである。

【図14】本発明に係わるナノ多孔質誘電体の多孔率と、金属原子に対するグリセロール分子の理論的なモル比を示すグラフである。

【図15】本発明の一実施例の時間に対する相対的な膜厚および相対的な膜の粘性を示すグラフである。

【図16】Aは本発明に係わるゾルーゲル薄膜処理装置の横断面図である。Bは本発明に係わるゾルーゲル薄膜処理装置の平面図である。Cは基板に接触する同じ装置の横断面図である。

【図17】Aは空になっている、本発明に係わる別の装置の横断面図である。Bは基板を収容する、本発明に係わる別の装置の横断面図である。

【図18】Aは空になっている、本発明に係わる別の装置の横断面図である。Bは基板を収容する、本発明に係わる別の装置の横断面図である。

【図19】本発明の別の特徴を示す別の装置の形状の横断面図である。

【符号の説明】

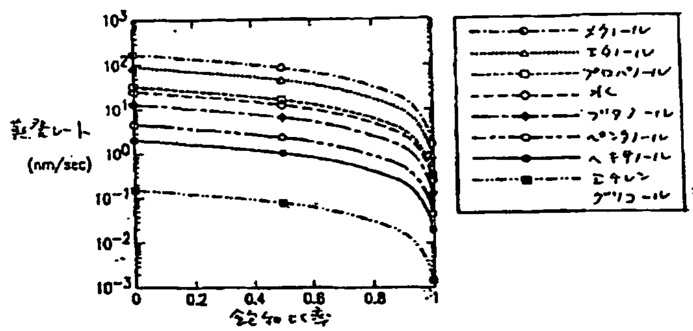
10　基板

12　導線

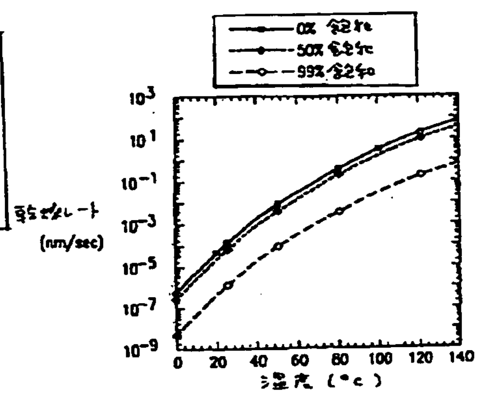
13　ギャップ

14　薄膜

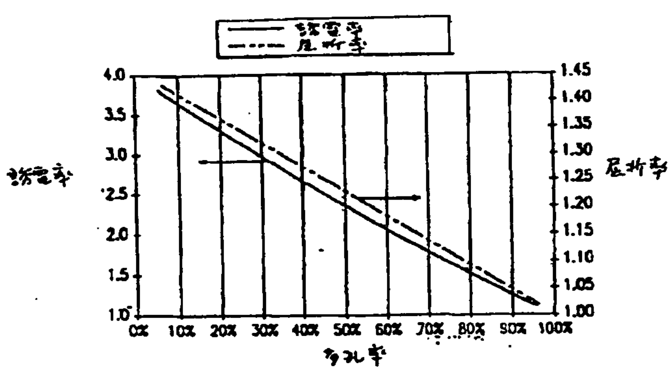
【図1】



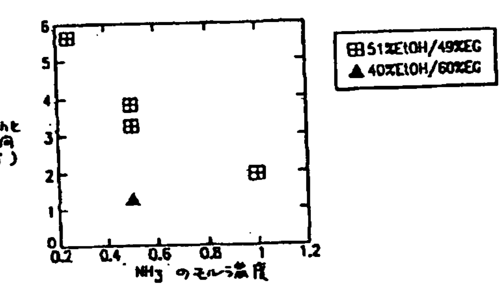
【図2】



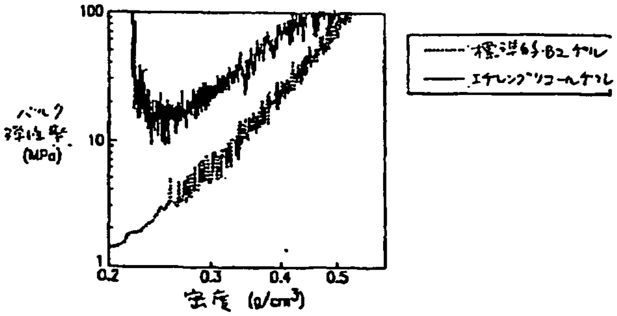
【図3】



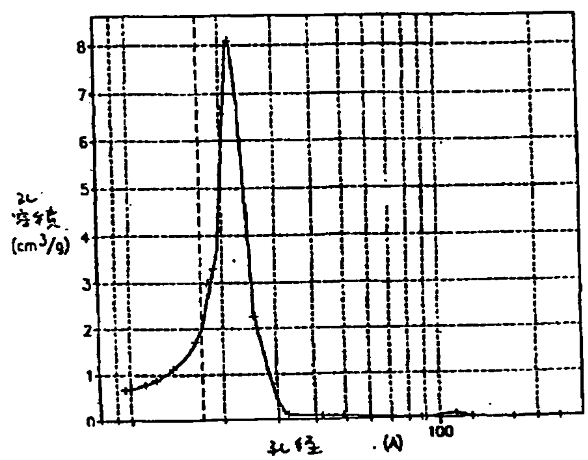
【図4】



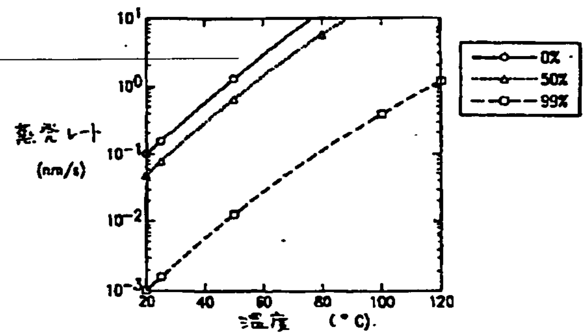
【図5】



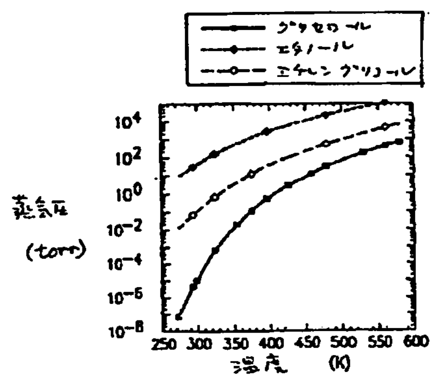
【図6】



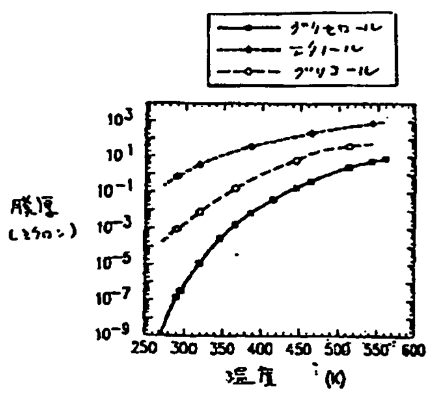
【図7】



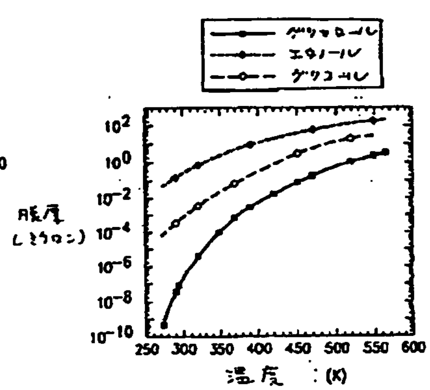
【図8】



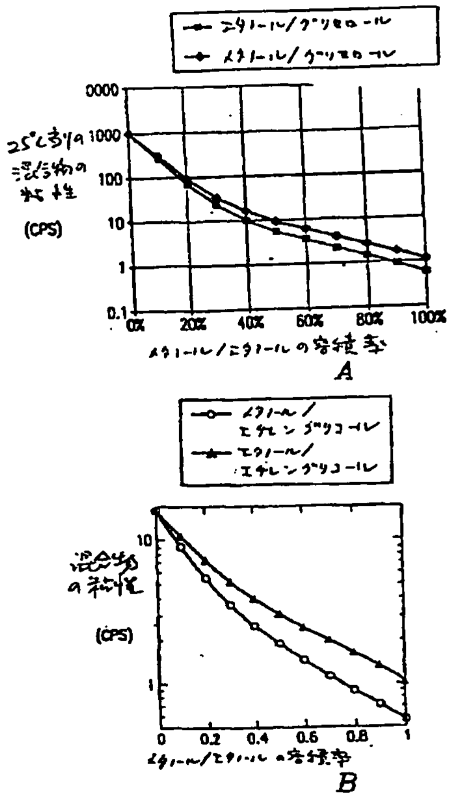
【図9】



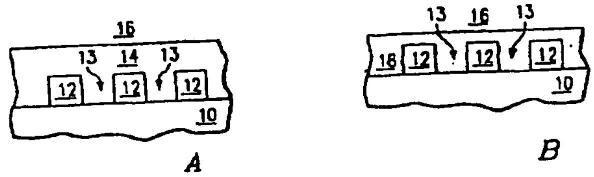
【図10】



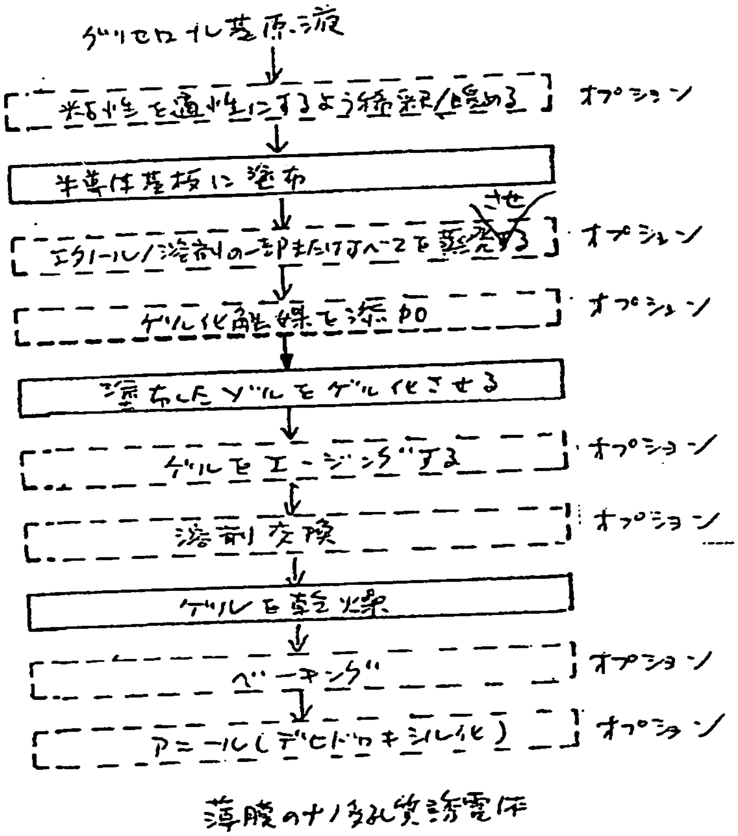
【図１１】



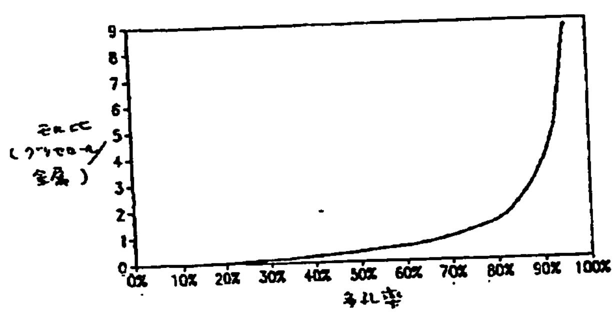
【図１２】



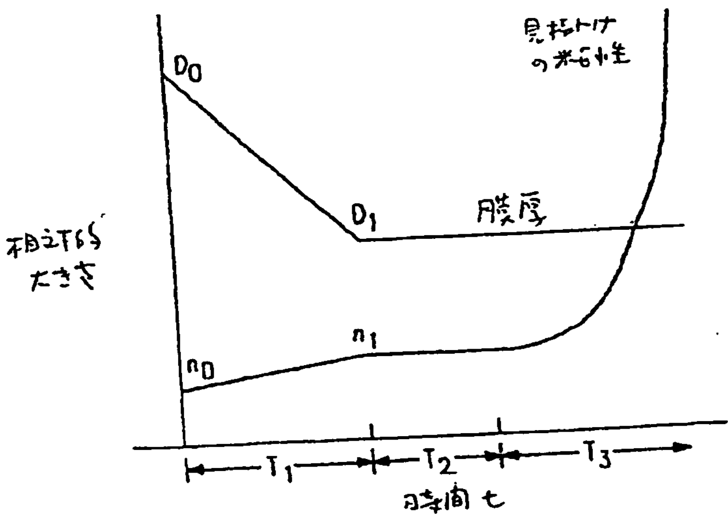
【図１３】



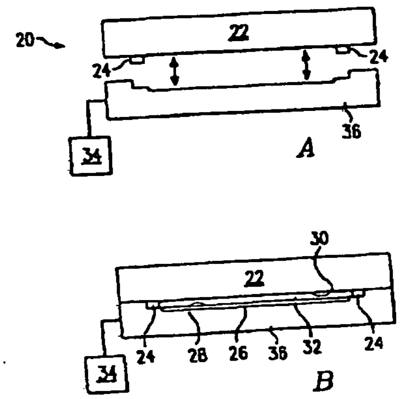
【図１４】



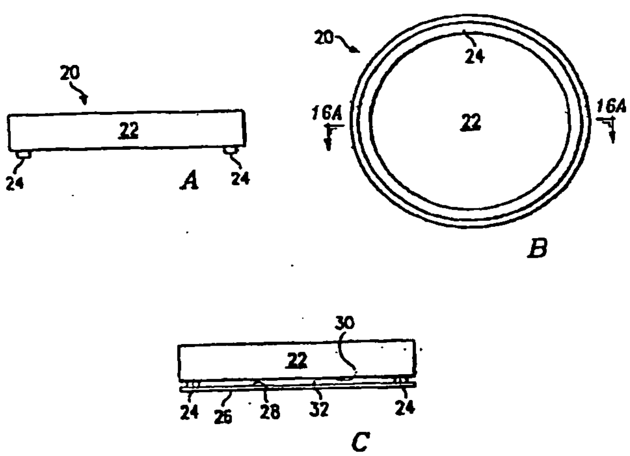
【図１５】



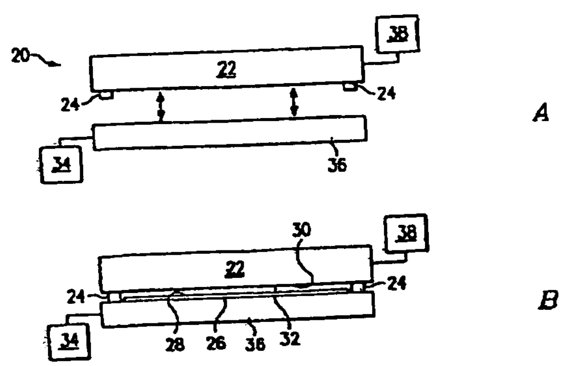
【図１７】



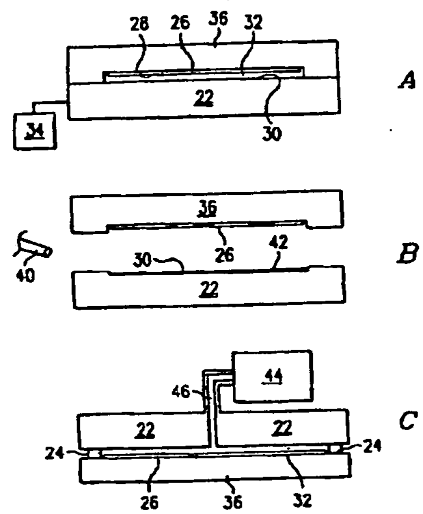
【図１６】



【図１８】



【図19】



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